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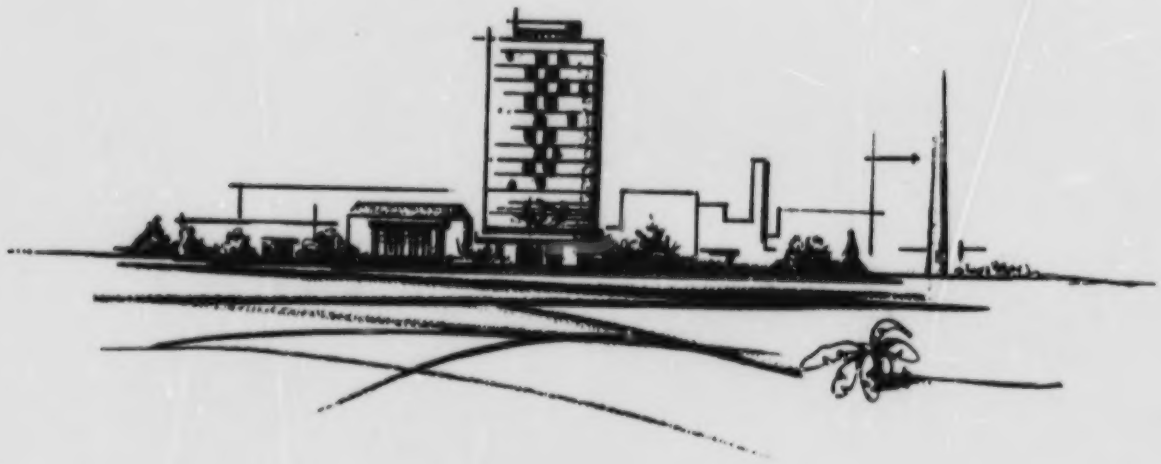
RESEARCH REPORT



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FINAL REPORT

on

ELECTRON MICROPROBE ANALYSIS OF ATMOSPHERIC AEROSOLS

to

NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
Contract CPA 22-69-33

December 31, 1969

by

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Columbus, Ohio 43201

MANAGEMENT SUMMARY

Contract No. CPA 22-69-33

"Electron Microprobe Analysis of Atmospheric Aerosols"

Background

This research program is designed to investigate the use of the electron microprobe for the determination of the fine structure and composition of airborne particulates of significance in air pollution studies. The results of this study should give NAPCA and others interested in air pollution a good overall picture of the applicability of the electron microprobe to small-particle analysis and characterization.

Significance of Research Results

The value of the electron microprobe for small-particle analysis has been demonstrated, and it has been shown that sample-collection techniques are presently the limiting factors in the amount of compositional information that can be obtained from small particles. A relationship between lead, bromine, and chlorine in automobile engine exhaust and atmospheric samples has been demonstrated and recommendations have been made regarding the type of instrumentation best suited for small-particle analysis.

Applications of Research Results

The data generated in the program show the many aspects where the electron microprobe can aid in small-particle analysis. The need for research in specimen preparation is necessary so that a sample is suitable for the particular requirements of the microprobe and other associated techniques. Further investigation of the chemical relationships of elements in air pollution particles is necessary to determine their effects on the environment.

TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	1
OBJECTIVES	2
EXPERIMENTAL WORK	2
Test Aerosols	2
Source Aerosols	8
Vehicle Exhaust	8
Automobile Exhaust, Stage 5, Beryllium Disk	8
Automobile Exhaust, Stage 4, Beryllium Disk	12
Automobile Exhaust, Stage 5, Electron Microscope Grid	12
Atmospheric Samples	15
Atmospheric Samples, Stage 4, Beryllium Disk	15
Atmospheric Samples, Stage 5, Beryllium Disk	15
Atmospheric Samples, Stage 2, Beryllium Disk	23
Atmospheric Samples, Stage 3, Beryllium Disk	27
Evaluation of Experimental Data	28
Energy Dispersive Analysis	29
CONCLUSIONS	32
RECOMMENDATIONS FOR FUTURE WORK	34
APPENDIX A	
GENERAL OUTLINE OF THE ELECTRON MICROPROBE POTENTIAL AND APPLICATIONS TO AIR POLLUTION RESEARCH	A-1

ELECTRON MICROPROBE ANALYSIS OF ATMOSPHERIC AEROSOLS

by

D. K. Landstrom and Doyle Kohler

SUMMARY

This report describes a research effort to determine the feasibility and capability of electron microprobe analysis as a method for obtaining detailed compositional and structural information about pollutant aerosol particles in the atmosphere. Extensive data is presented from known test aerosols, automobile engine exhaust, and atmospheric samples. It was determined that the sampling method is presently the limiting factor in the detection and analysis of small particles, and, by preparing samples to minimize X-ray background, particles as small as 0.1 micron can be successfully analyzed. The theoretical limitations of the microprobe for both wavelength-dispersive and energy-dispersive spectrometers are discussed, and recommendations are made about analysis systems for small particles.

INTRODUCTION

The problems associated with air pollution are well known and are becoming increasingly more important as the population and industrial activities expand. The effects of suspended particulates in the air can be observed every day and include soiling, deterioration of materials, corrosion, smog, and physiological reactions. Other long-term effects not so readily observable also are a direct result of particulate contamination. Actually, very little is known about the composition and fine structure of individual airborne particles, especially those in the size range from about 1 micron in diameter and below.

Some of the classical methods of analysis such as dustfall estimates, total suspended matter, particle size, or gross chemical analysis often do not provide enough information about individual particles. Even such valuable techniques as X-ray diffraction, X-ray fluorescence, electron microscopy, light microscopy, mass spectrometry, and many others do not provide compositional data on very small individual particles except in a very few special cases. It is the analysis of single selected particles that presents both an opportunity and a challenge for expanding the information available about the effects of air pollution. Very little is known about the effects of individual particles on people, plants, animals, or objects. Often, particles of interest may be present in specific particle size ranges, but very little is known about what particle size range can be expected for a given composition. In many cases, a single particle of interest may be lost among thousands of particles that may be harmless or of no particular interest. In atomic energy operations, the detection of just one particle of fissionable material among many other particles could be of major importance, especially from the health physics standpoint. The electron microprobe analyzer appears to have great promise as a method for the analysis of individual particles in the micron range.

A discussion of the problems and theoretical considerations of the electron microprobe as applied to small-particle analysis is important to the work described here. Because this discussion is so extensive, it has been written separately as an Appendix.

OBJECTIVES

The research program described herein was planned to achieve the objectives set forth by the National Center for Air Pollution Control to determine the capacity of electron microprobe analysis as a method for obtaining detailed compositional and structural information about pollutant aerosol particles in the urban atmosphere and from specific sources. More specifically, the major objectives of the program were to perform, through electron microprobe analysis, detailed nondestructive chemical analysis of aerosol particles collected from the ambient atmosphere and from specific sources, and thereby define the types of quantitative and qualitative information about aerosol fine structure and composition obtainable with the present state of the art. The study should demonstrate the sensitivity and the limitations of the method, provide information on the importance of instrumental design parameters, and outline future capabilities as projected from the present state of the art.

EXPERIMENTAL WORK

This program on "Electron Microprobe Analysis of Atmosphere Aerosols" was expected to begin on January 1, 1969, and continue for 6 months. Due to delays principally in receiving samples appropriate for the study, no technical work other than that of a survey nature was performed on this contract until April, 1969, and the overall time period of the program was extended to 12 months.

The first samples were delivered on March 27, 1969, and consisted of known test aerosols as will be described below. Results were reported in a letter report dated July 1, 1969, and are summarized below.

Test Aerosols

Two sets of samples collected from Stages 2, 3, 4, and 5 of a Battelle cascade impactor were received and consisted of aerosols of NaCl and $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$, respectively. Two types of collections were received for each aerosol, one using polished beryllium disks for a substrate and the other using Formvar-coated electron microscope grids.

Results obtained on the NaCl beryllium-disk samples were generally good, and pictures showing the location and elemental distributions were obtained for all four cascade impactor stages. These samples also allowed a comparison of a new-type combination scanning electron microscope/microprobe (Materials Analysis Company Model 400S) with an older, more conventional microprobe (Materials Analysis Company Model 400). The superior performance of the 400S is clearly indicated by a direct

comparison of photographs obtained of identical sample areas in the two instruments. Figure 1 is a back-scattered electron (BSE) image taken on the older microprobe showing several particles from Stage 2 of the cascade impactor. Figures 2 and 3 are X-ray distribution photographs of the sodium and chlorine, respectively, in the same area as shown in Figure 1. These figures should be compared with Figures 4 and 5, which show the BSE and the chlorine X-ray images respectively, of the same sample. (Note the slightly lower magnification of Figures 4 and 5.) Comparison of these figures clearly show the superior resolution obtained in the new microprobe. Note also the better X-ray resolution shown in the chlorine picture.

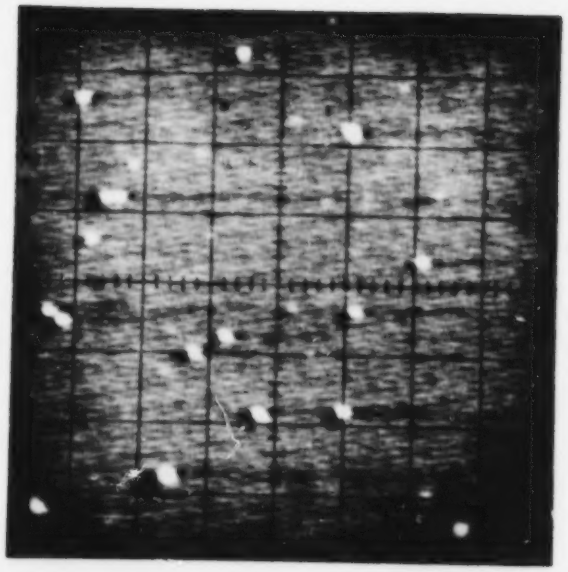
As is mentioned in the general discussion on microprobe analysis (Appendix) instrumental conditions are important for maximum particle resolution. Figures 6 and 7 illustrate the effect of beam current on the resolution. (Higher beam currents cause the beam to expand in size.) Figure 6 is a BSE image taken at a specimen current of 0.009 μa. Note that Figure 6 represents the same area as in Figures 1 and 4, except at higher magnification. Figure 7 is a similar photograph taken at 0.03 μa (normal operating conditions for X-ray analysis). It is clear that there is a loss of resolution in Figure 7 as well as a smearing effect that makes the particles appear larger than they actually are. A rate-meter scan of this same area for chlorine using the same instrument conditions as for Figure 7 is shown in Figure 8.

A useful limit of magnification for this type of scanning electron microprobe where the beam diameter is on the order of 0.1 to 0.2 micron is approximately 1000-3000X. Figure 9 shows three of the particles from Stage 2 of the cascade impactor at 3000X. At this magnification, very little structure is observable, and the surface detail of this type of specimen would have to be studied in a scanning electron microscope for proper resolution. The X-ray sensitivity is still good at this magnification; Figures 10 and 11 show the distribution of Na and Cl, respectively. Note the higher noise level (background counts) in the Na distribution, due to a less favorable peak-to-background ratio for this element in our microprobe. Figures 9, 10, and 11 represent a practical limit for this type of specimen preparation and our particular commercial microprobe.

In general, the samples obtained on electron microscope grids were not as satisfactory as those on beryllium disks. The instrument conditions necessary for X-ray analysis usually caused the support film to buckle or melt. Figure 12 is a BSE image obtained from the Stage 2 cascade impactor sample. It is interesting to note that the NaCl cubic shape is visible on these samples, whereas those on the beryllium-disk samples are generally spherical or oval in shape. If the beryllium-disk had been exposed to more atmospheric moisture than the grid samples, the shape differences could be explained as due to the increase in moisture.

Particles were detected and analyzed from Stages 3, 4, and 5 on the beryllium disks; but the picture quality of these was progressively worse from those presented for Stage 2 and, because of the difficulty of reproduction, micrographs are not included here. Sodium and chlorine could be detected in particles that were not visible optically but which could be detected by the scanning electron beam system of the microprobe. There was some agglomeration of particles on Stages 3, 4, and 5 that gave relatively high Na and Cl counts, while the smallest particles (approximately 0.1 to 0.2 μ in diameter) gave only a few counts above the background level.

Figure 13 illustrates one method of detecting particles that is often more sensitive than the standard BSE image. This method of data presentation is called oblique projection (OP) and consists simply of modulating the y-deflection of the oscilliscope with



430X

FIGURE 1. BACK-SCATTERED ELECTRON IMAGE OF SAMPLE FROM STAGE NO. 2 OF CASCADE IMPACTOR (NaCl Be DISK) MODEL 400 MICROPROBE

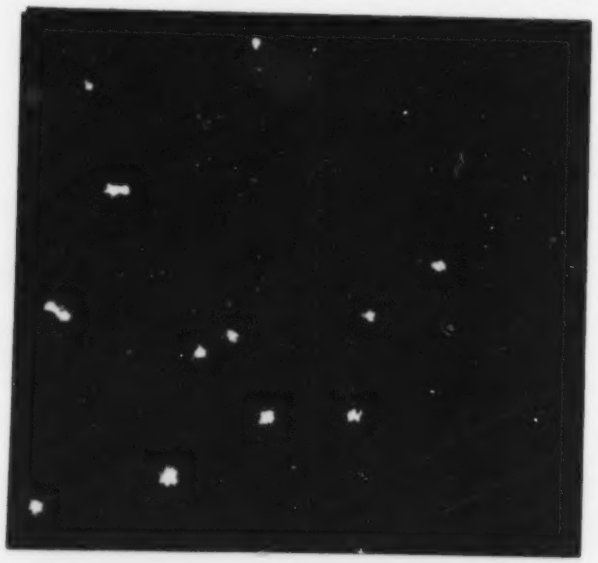


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FIGURE 3. CHLORINE DISTRIBUTION IN THE SAME AREA AS FIGURE 1 AND 2
Pulse Mode, Model 400 Microprobe

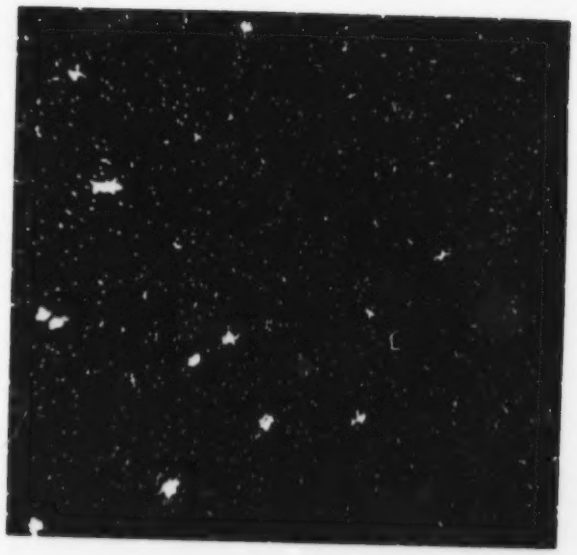

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FIGURE 2. SODIUM DISTRIBUTION IN THE SAME AREA AS FIGURE 1
Rate Meter Mode, Model 400 Microprobe

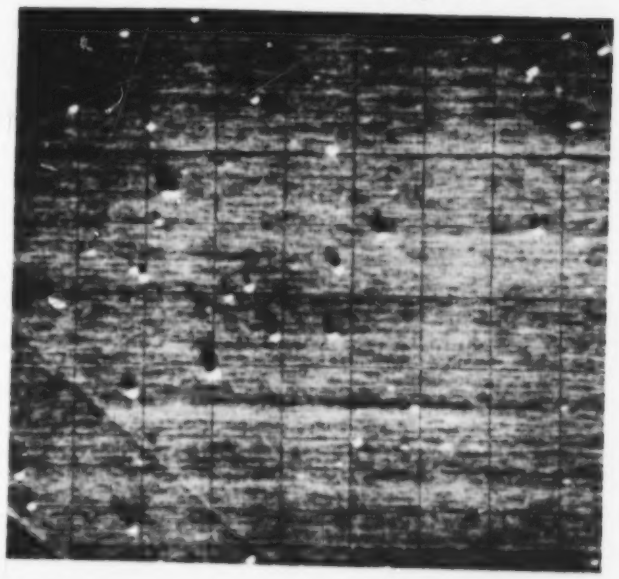

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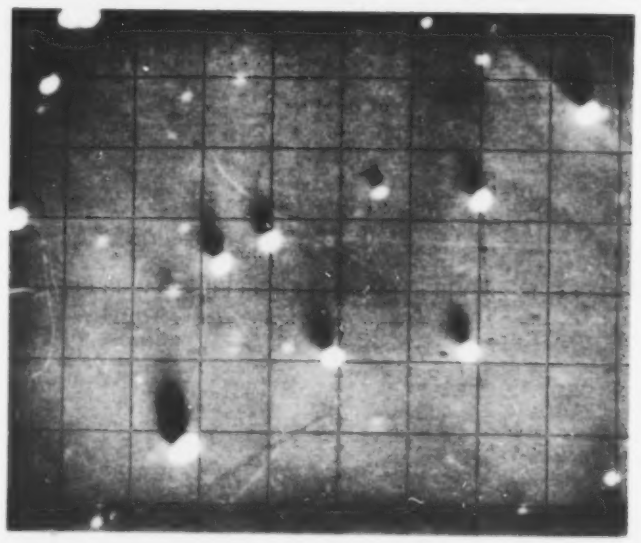
FIGURE 4. BACK-SCATTERED ELECTRON IMAGE OF SAMPLE FROM STAGE NO. 2 OF CASCADE IMPACTOR (NaCl Be DISK) MODEL 400S SCANNING ELECTRON MICROPROBE

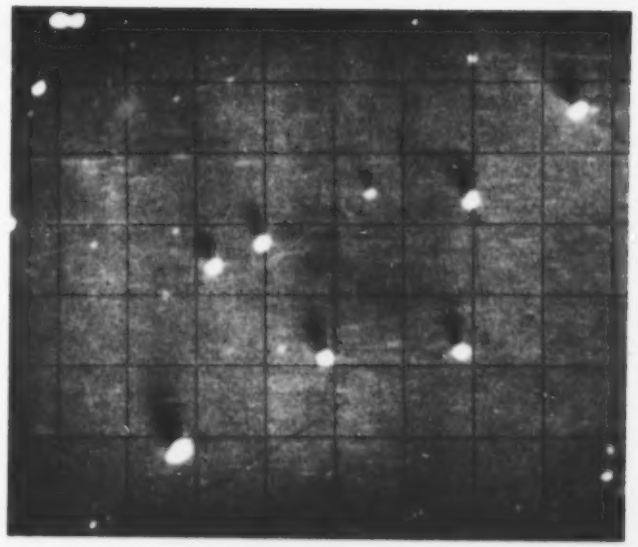
300X

FIGURE 5. CHLORINE DISTRIBUTION IN THE SAME AREA AS FIGURE 4
Rate Meter Mode, Model 400S Scanning Electron Microprobe



700X

FIGURE 7. SAME AS FIGURE 6 EXCEPT TAKEN AT 0.03 μAMP SPECIMEN CURRENT

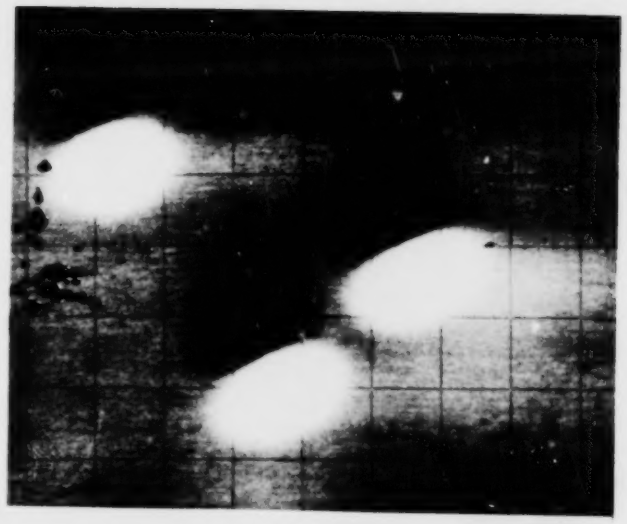


700X

FIGURE 6. BACK-SCATTERED ELECTRON IMAGE OF SAMPLE FROM STAGE NO. 2 OF CASCADE IMPACTOR (NaCl Be DISK) MODEL 400S
Taken at 0.009 μAMP Specimen Current

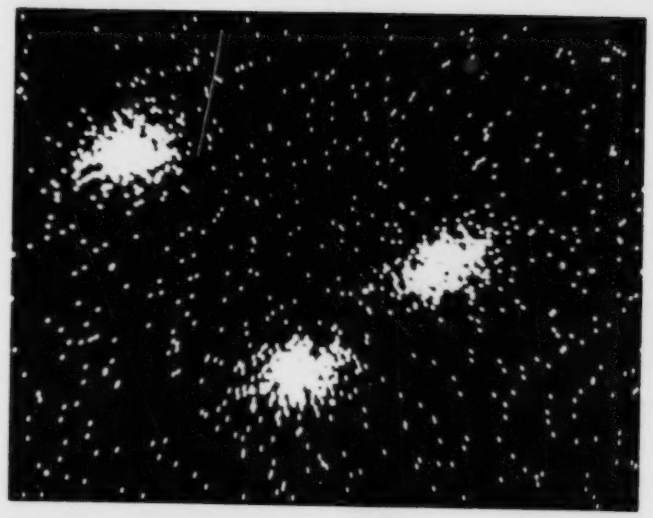
700X

FIGURE 8. CHLORINE DISTRIBUTION IN THE SAME AREA AS FIGURE 7
Rate Meter Mode, Model 400S



3000X

FIGURE 9. BACK-SCATTERED ELECTRON IMAGE OF SAMPLE FROM STAGE NO. 2 OF CASCADE IMPACTOR (NaCl Be DISK) MODEL 400S



3000X

FIGURE 10. SODIUM DISTRIBUTION IN THE SAME AREA AS FIGURE 9

Rate Meter Mode, Model 400S

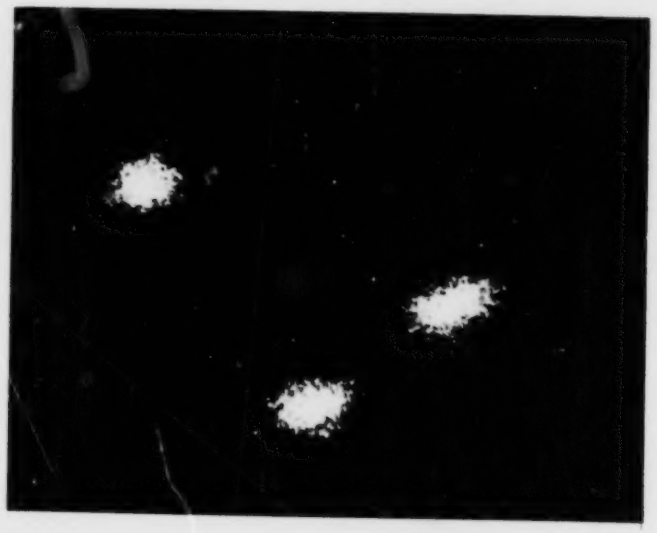


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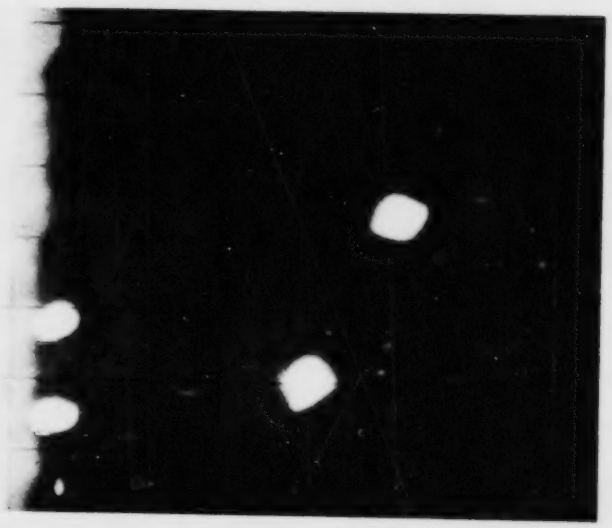
FIGURE 11. CHLORINE DISTRIBUTION IN THE SAME AREA AS FIGURE 9 AND 10

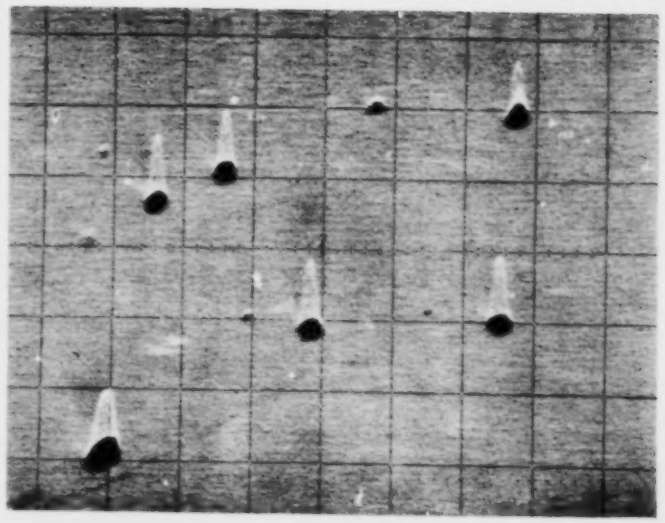
Rate Meter Mode, Model 400S



2000X

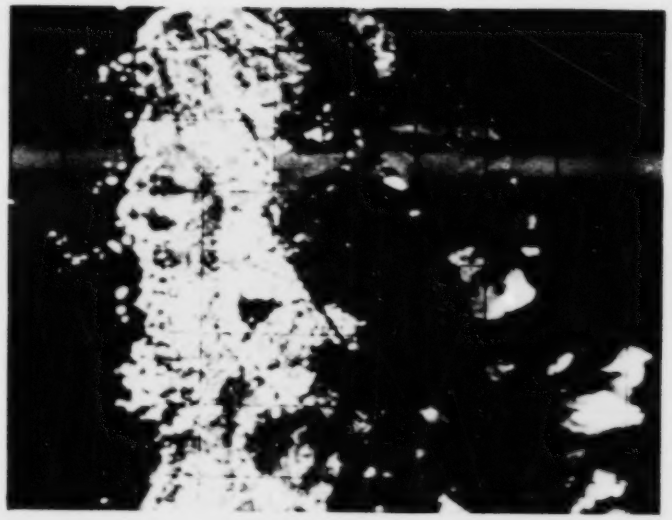
FIGURE 12. BACK-SCATTERED ELECTRON IMAGE OF SAMPLE FROM STAGE NO. 2 OF CASCADE IMPACTOR

NaCl Electron Microprobe Grid



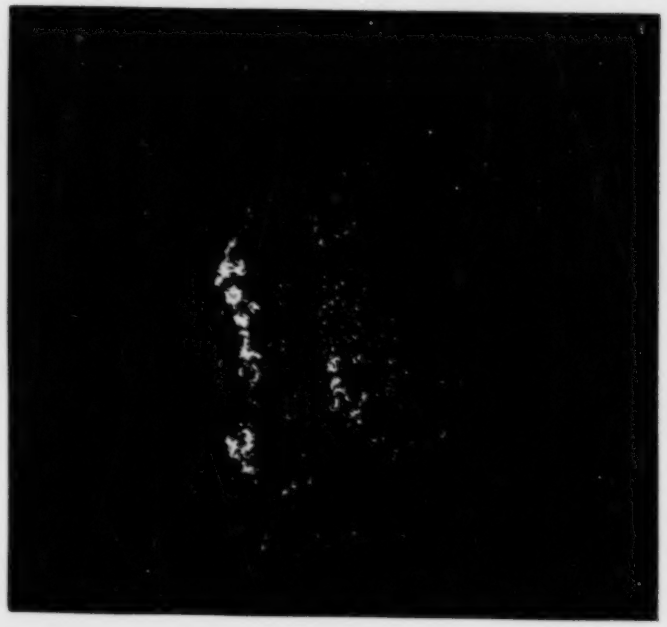
1000X

FIGURE 13. OBLIQUE PROJECTION MADE OF SAMPLE FROM STAGE NO. 2 OF CASCADE IMPACTOR (NaCl Be DISK)



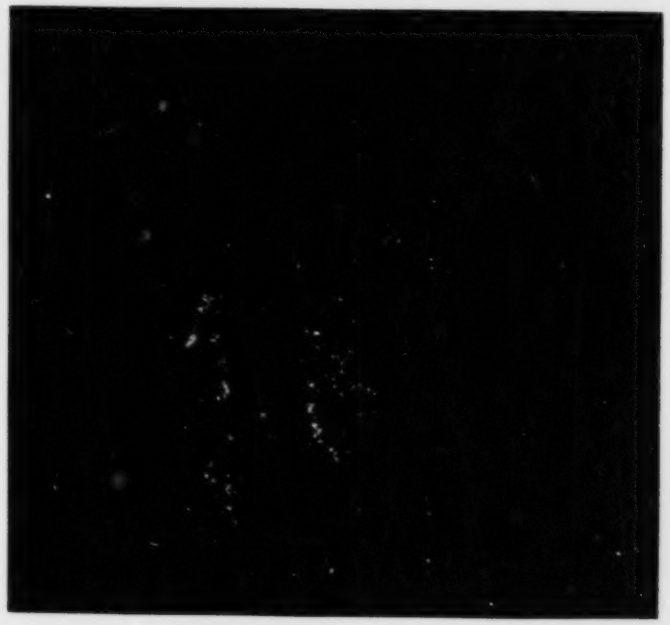
200X

FIGURE 14. BACK-SCATTERED ELECTRON IMAGE OF SAMPLE FROM STAGE NO. 4 OF CASCADE IMPACTION (AUTO EXHAUST, Be DISK) SHOWING PARTICLES IN SCRATCH



200X

FIGURE 15. LEAD DISTRIBUTION IN THE SAME AREA AS FIGURE 14



200X

FIGURE 16. CHLORINE DISTRIBUTION IN THE SAME AREA AS FIGURE 14

the BSE signal or the specimen current. The ordinary BSE image is produced by modulating the Z axis (spot intensity). Thus, in the oblique projection mode, very small changes in the back scattered signal that might not be observable in the regular image can be easily observed. Topographical detail is also enhanced, although interpretation of the image is often difficult.

The $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ samples were all unsatisfactory for probe analysis. The sample area could not be located in the light microscope or by a scanning electron image. Some isolated clumps of material were found, but these appeared to be debris or contamination on the beryllium surface. Consequently, no further work was carried out on these samples.

Source Aerosols

Vehicle Exhaust

In April, 1969, some automobile engine exhaust samples were received, and early microprobe results on them were not encouraging. In these early samples, only gross quantities of carbon could be detected, with traces of Si, Ca, Fe, and Cl. No lead was detected, which was quite surprising to us since engine exhaust samples we had prepared here under another program all showed easily detectable lead. At first, it was thought that the particle collection time was not sufficient, and, indeed, this seemed to be part of the problem; however, when later samples were received (June, 1969) the same lack of definitive particles was noted. It was evident that there was a definite sampling problem; the beryllium disks simply were not retaining the impinging particles as they should, and this was partially confirmed by one of the samples that was received at this time.

A beryllium disk from Stage 4 of the Battelle cascade impactor was examined and very few particles were found, with the exception of one area where a large amount of lead was detected. This area is shown in Figure 14, which is a BSE image of this area. Close inspection of this region showed that this area was a surface scratch on the beryllium plate and that this was the reason that the particles were trapped. Chart scans and photographs were obtained of this area, with Figures 15 and 16 showing the distribution of lead and chlorine, respectively, in the same area as of Figure 14. Photographs were also obtained showing the Si, Fe, Cr, Mn, and Ni distribution in this area, but they are not included in this report. Many Si particles were observed as well as many Fe particles. One fairly large particle ($\approx 20\mu$, near arrow in Figure 14) was positively identified by quantitative analysis to be type 304 stainless steel.

In October, 1969, the first automobile exhaust samples were received that were useful for extensive investigation. Acting on our suggestion, NAPCA had put a very thin coating of silicone grease on the surface of the beryllium disks to aid in particle capture and, in addition, had used a longer sampling time. These samples were very good for microprobe analysis, and the results are reported below.

Automobile Exhaust, Stage 5, Beryllium Disk. The deposit from the cascade impactor was contained in one small spot near the center of the beryllium disk. Unlike previous samples, no difficulty was experienced in locating the deposit area, which appeared to be a thick agglomeration of particles that thinned out toward the edges of the deposit. Near the edges and surrounding area, individual particles could be detected, although many of the larger ones appeared to be made up of clumps of many smaller particles.

TABLE 1. RELATIVE CONCENTRATIONS OF ELEMENTS DETECTED IN AUTOMOBILE EXHAUST SAMPLES

H = high, M = medium, L = low, T = trace, ND = not detected.

Sample Description	Element											
	Pb	Cl	Br	Al	Zn	Fe	S	P	Si[a]	Ca	Cu[b]	K[b]
Stage 5, Be disk, random area	H	H	H	M	M	M	L	L	M	M	ND	ND
Stage 4, Be disk, random area	H	M	M	M	L	M	L	L	H	L	ND	ND
Stage 4, Be disk, high iron	L	L	T	ND	T	H	T	L	H	L	ND	ND
Stage 4, Be disk, high zinc, type 1	M	M	L	ND	H	L	T	T	L	L	H	T
Stage 4, Be disk, high zinc, type 2	L	L	L	ND	H	L	T	T	L	L	T	T
Stage 4, Be disk, high lead	H	H	H	ND	T	L	T	T	H	L	ND	ND
Stage 5, EM grid, random area	H	L	H	ND	T	L	L	L	ND	L	H[c]	ND

(a) Silicon is present in trace amounts from the silicone grease used to coat the beryllium disks; however, readings were taken from the beryllium metal without deposit and subtracted from the readings obtained in the deposit area.

(b) Usually only with zinc particles.

(c) From electron microscope grid.

In order to obtain a general idea of the deposit composition, the electron microprobe beam was positioned in the densest portion of the deposit and a wavelength scan for all detectable elements was run.* Table 1 gives a summary of the elements detected in all of the automobile exhaust samples and presents a very rough estimation of the relative concentration of the various elements.

A BSE image of the deposit area was obtained (Figure 17) and individual X-ray line scans for Pb, Si, S, Fe, Ca, Al, Zn, P, Br, and Cl were made along the line visible in Figure 17. These profiles were taken directly from the oscilliscope screen of the microprobe at various scale factors, so the intensities (peak heights) of the scans are not directly comparable. The scans do provide a general idea of the elemental distributions, and it is easy to see, for example, the obvious segregation of individual particles containing iron. The lead, bromine, and chlorine are all fairly evenly distributed in the deposit; the Ca, Si, Al, S and, to a lesser extent, the Zn and P show some evidence of segregation into individual particles.

Chart scans for each of these elements along the scan line of Figure 17 were also obtained which provide greater details than it is possible to obtain with an oscilliscope profile. The chart scans confirm the indications shown on the X-ray line scans and also show the deposit to be less dense at the center; i.e., the deposit is somewhat ring-shaped. Due to the difficulty of reproduction, the chart scans are not included in this report but are available for study if desired.**

An area near the edge of the deposit was located and BSE pictures at 1000X of some scattered individual particles were obtained. X-ray distribution photographs were obtained for Pb, Cl, Br, Zn, Fe, P, and Si. No photographs for S and Ca were obtained, since these elements were found only in heavier regions of the deposit. These photographs show that areas high in lead are also high in chlorine and bromine. Phosphorus, zinc, and aluminum also appear to be associated with these areas. The calcium, iron, and silicon seemed much more segregated and not necessarily associated with high-lead areas.

An attempt was made to obtain more nearly quantitative data from this sample; Table 2 shows the results for two of the stages. Obviously, these values will not total 100 percent, since there are large quantities of hydrogen, nitrogen, and oxygen associated with these deposits and these were not determined. The carbon value is probably low due to large absorption effects from the lead in the deposit.

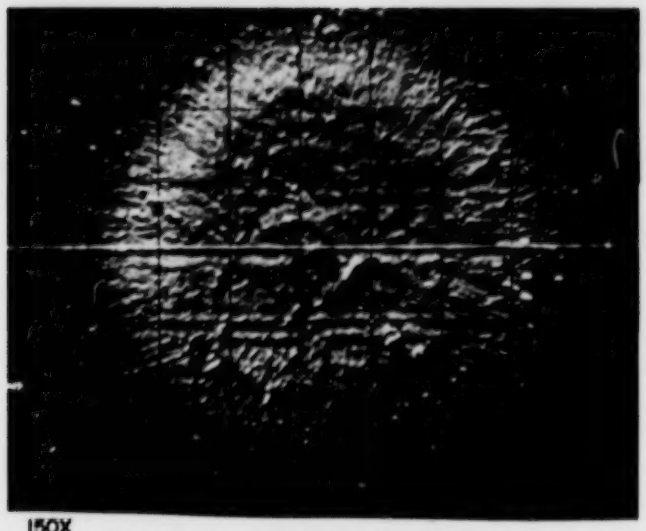
TABLE 2. SEMIQUANTITATIVE ANALYSIS OF AUTOMOBILE EXHAUST SAMPLES ON BERYLLIUM DISKS

Sample Description	Element (weight percent)										
	Pb	Cl	Br	Al	Zn	Fe[a]	S	P	Si[b]	Ca	C
Stage 5, Be disk	17.6	2.7	4.3	1.0	3.5	0.2	0.3	0.5	4.1	0.2	11.5
Stage 4, Be disk	14.3	1.0	1.7	1.2	Trace	0.8	0.7	0.3	8.1	1.0	10.0

(a) Highly segregated – higher values obtainable on individual particles.
(b) Background from silicone grease subtracted.

*Due to the difficulty of reproducing wavelength chart scans (which may be 4 to 6 feet long), none of the charts are included in this report. Results will be summarized, and reference to the original charts can be made if questions arise.

**Chart scans were obtained for all of the samples documented in this report. None are included for the reasons mentioned above but are on hand for study if desired. In general, the chart scans provide greater resolution and greater accuracy in locating specific particles, hence were mainly used to pick specific particles for analysis.



150X

B.S.E. Image Showing Scan Line

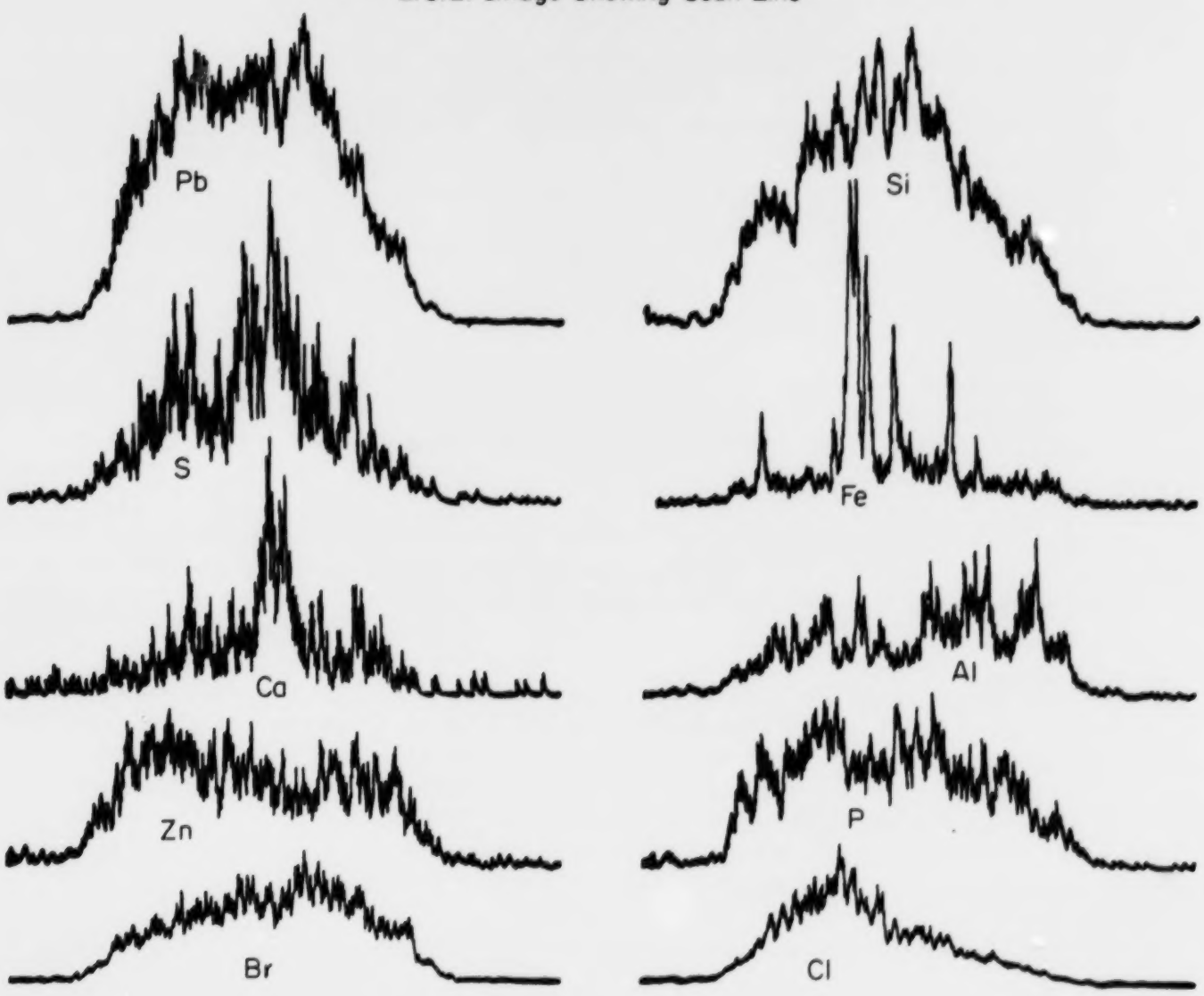


FIGURE 17. X-RAY SCANS ALONG LINE SHOWN IN PHOTOGRAPH, STAGE 5, Be DISK, AUTOMOBILE EXHAUST

Comparisons between the two stages are quite interesting, and it is easy to see that the larger, more segregated particles (Fe, Si, and Ca) are higher on Stage 4 than on Stage 5; the Pb, Cl, Br, and Zn, which appears to be related to smaller particle size, are higher on the Stage 5 sample. It would be interesting to see what type of elemental separation (by particle size) would be possible using the other stages of the cascade impactor. Unfortunately, no other stages were supplied, so complete comparisons are impossible. It could be conjectured that the cascade impactor might be useful for separation purposes, not only on a particle-size basis, but on an elemental basis if specific elements are present in certain size ranges. This could be quite important in some analytical techniques where, for maximum sensitivity, elements of little or no interest could be eliminated or greatly reduced in the analyzed sample.

Automobile Exhaust, Stage 4, Beryllium Disk. The deposit area on this sample appeared slightly less dense than that obtained on Stage 5. A greater number of individual particles were also visible in this sample. As in the case of Stage 5, a wavelength scan for all detectable elements was run on a representative area, and the results are similar. Relative concentrations for Stage 4 can be found in Table 1.

A BSE image of the deposit was obtained (Figure 18) and individual X-ray line scans for Pb, Fe, Al, Br, Zn, S, Si, Cl, P, and Ca were made along the line visible in the photograph. Again, the heights of the traces are not directly comparable, but provide only a relative elemental distribution along the scan line. Elemental segregation is easier to see in this sample than in the Stage 5 samples.

Chart scans along the scan line of Figure 18 were also obtained but are not included in this report. Segregation of Fe, Si, Ca, Zn, and, to a less extent, Pb, Cl, Br, and S can be clearly shown in these charts.

An area near the edge of the deposit was located and BSE and elemental distribution pictures were obtained for Pb, Br, Si, Fe, Cl, Zn, and Cr. The S, P, and Al were not intense enough to provide a good picture. These pictures are not included in this report.

Since individual particles could be found easily in this sample, particles with high values of various elements were located and individually analyzed with a wavelength scan. The results are summarized in Table 1 and include particles having high iron, high zinc, and high lead content.

Several particles containing high sulfur content were found in this sample and a sulfur wavelength-shift measurement was made. Figure 19 shows the sulfur spectrum from the sample compared with the spectrum from PbS and $CaSO_4$. In general, Figure 19 shows that most of the sulfur present in this sample is in the sulfate form. There is a reproducible double peak in the sample spectrum that might indicate a small percentage of elemental sulfur; however, this could not be confirmed without extensive additional work with better standards and spectrometer alignment.

Semiquantitative data for this sample are given in Table 2.

Automobile Exhaust, Stage 5, Electron Microscope Grid. The deposit on the microscope grid was quite thick and had the same ring structure as was visible on the Stage 5 beryllium-disk sample. A wavelength scan on the thick deposit area was obtained, with the relative concentrations for this sample summarized in Table 1.

B.S.E. Image Showing Scan Lines

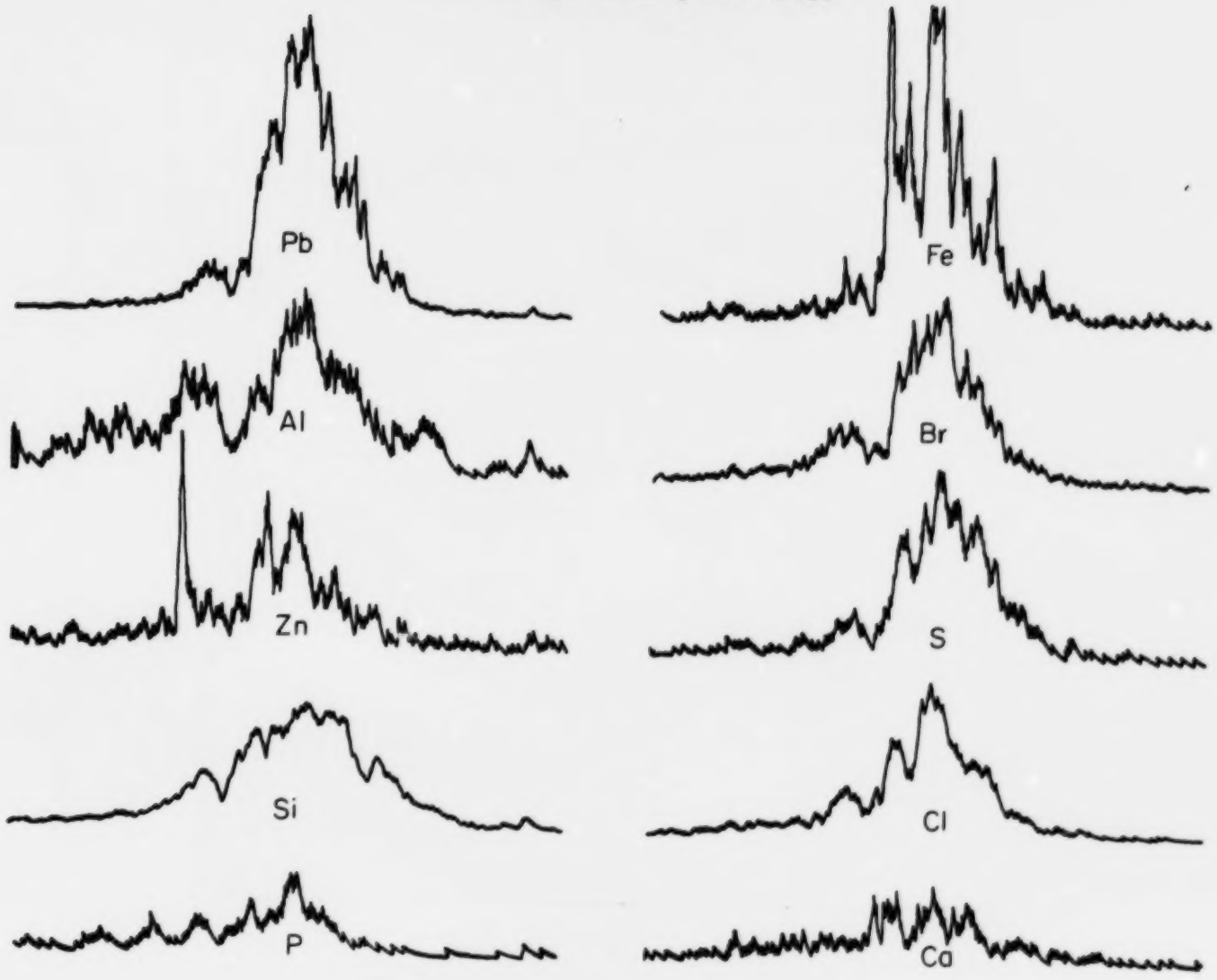


FIGURE 18. X-RAY SCANS ALONG LINE SHOWN IN PHOTOGRAPH, STAGE 4, Be DISK, AUTOMOBILE EXHAUST

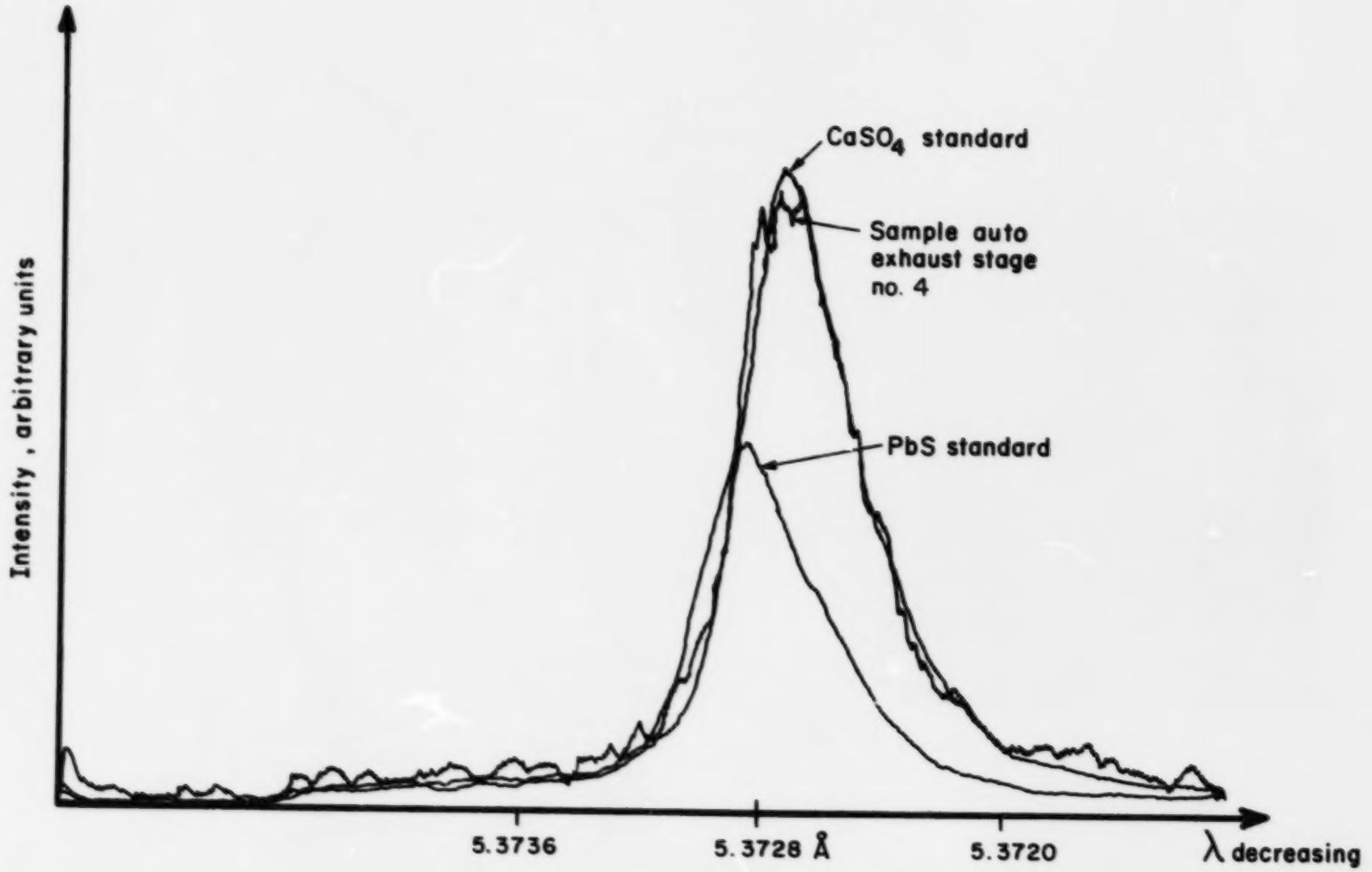


FIGURE 19. ELECTRON MICROPROBE ANALYSIS OF AUTOMOBILE EXHAUST – SULFUR WAVELENGTH SHIFT

A BSE image of the deposit was obtained (Figure 20) and individual X-ray line scans for Cl, Pb, Br, Al, S, Fe, Zn, Si, Ca, and P were made along a line which is visible in the photograph. Segregation of some of the elements is clearly visible.

Areas near the edge of the deposit areas were examined for individual particles, but there was no area defined clearly enough to obtain suitable photographs.

Atmospheric Samples

Atmospheric Samples, Stage 4, Beryllium Disk. This sample deposit was much lighter than those obtained for the automobile exhaust samples, but it still was quite adequate for analysis. Most of the samples was concentrated in a half circle and contained many individual particles scattered over the beryllium surface.

Initially, the beam was positioned in the densest portion of the deposit and a wavelength scan for all detectable elements was run. Table 3 is a summary of the elements detected in this sample and all of the other atmospheric samples. No attempt was made to obtain quantitative data in other than relative terms.

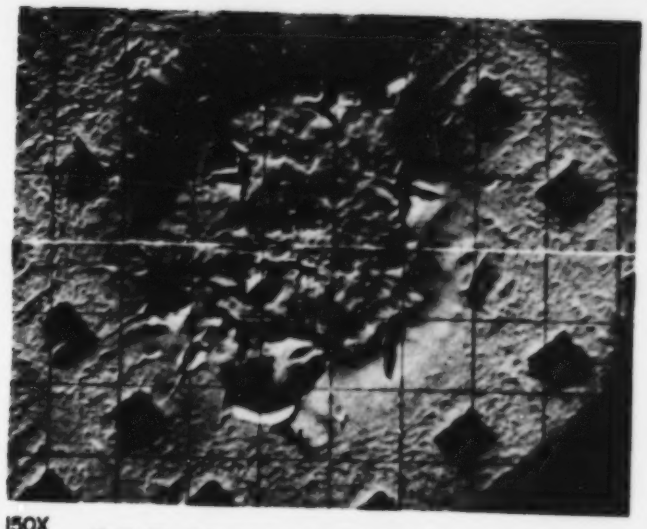
A BSE image of the deposit area was obtained (Figure 21) along with individual X-ray pulse mode pictures for Pb, Si, Br, Zn, Fe, Mn, Ca, S, Cl, K, and Al (Figure 22 through 32, respectively). Since these pictures are typical of those obtained for all the other samples, only this set is reproduced; however, simular photographs were obtained on all of the atmospheric samples. Segregation of some of the elements is quite evident.

Individual particles with high iron, high zinc, high lead, and high calcium contents, respectively, were easily located in this sample, and wavelength scans were obtained. The data are summarized in Table 3. BSE images and X-ray distribution photos were also obtained for each of these particles but are not included in this report. The high calcium particle (Stage 4, Table 3) is interesting to examine since the wavelength scan of this particle shows trace amounts of tin, titanium, and chromium. It is important to realize that, unless specific elements are sought or particle analysis is performed on an individual and systematic basis, elements which are present in only a few particles can easily be missed in an analysis. This aspect is covered more fully in the Appendix.

This atmospheric sample was extensively examined for lead particles that had no bromine or chlorine associated with them, but none could be found; i.e., all particles containing lead also contained bromine and chlorine, as was also true of the automobile exhaust samples.

Many particles were found in which no elements could be detected, and these were probably hydrocarbon deposits.

Atmospheric Samples, Stage 5, Beryllium Disk. The deposit area of this sample appeared to be a uniform circle slightly less dense in the center. The beam was focused on a dense, representative area of the deposit and a wavelength scan was made. The results are show in Table 3. It is interesting that this random area contained fewer detectable elements than did the sample from Stage 4 (random area, Table 3).



150X

B.S.E. Image Showing Scan Line

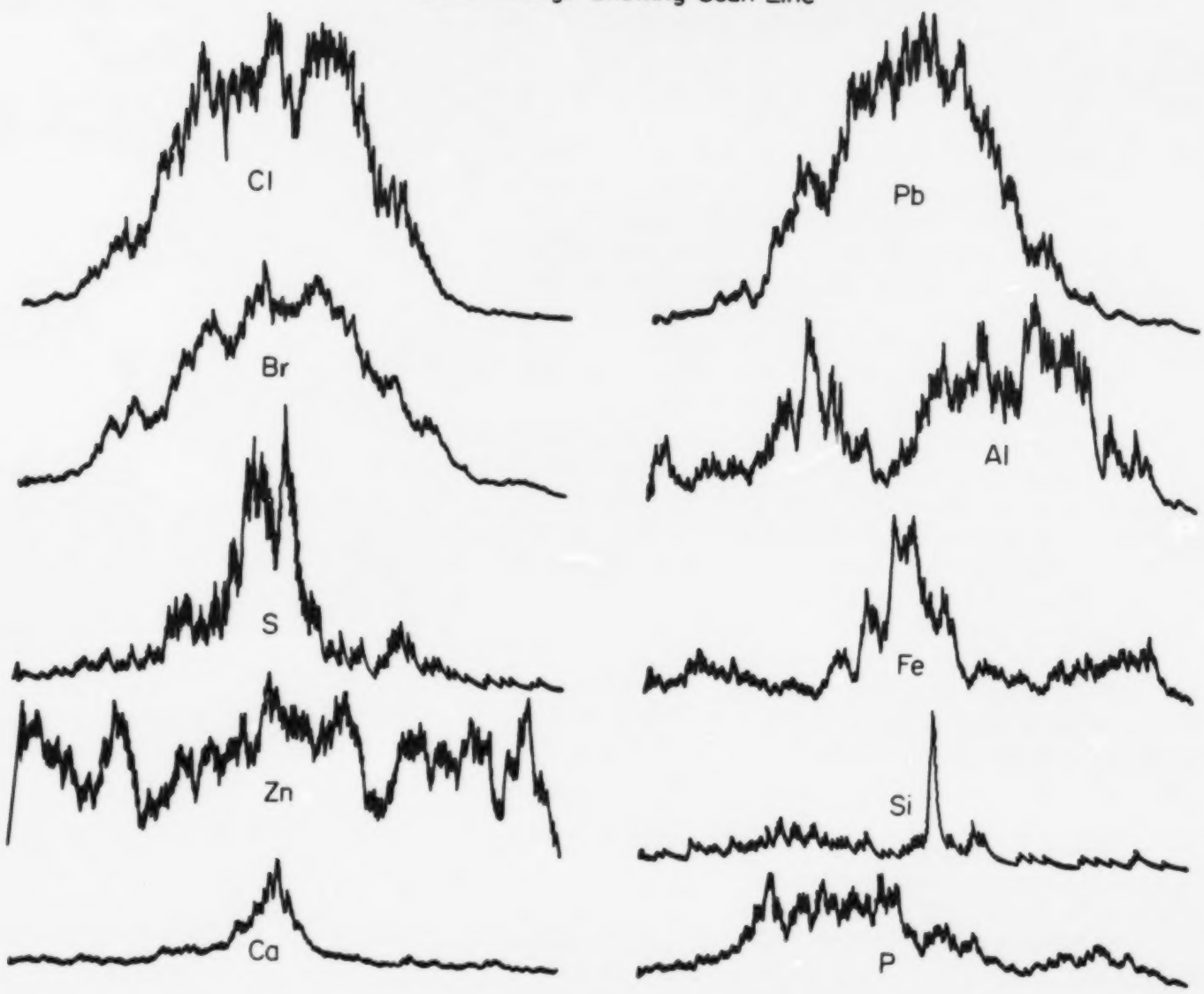


FIGURE 20. X-RAY SCANS ALONG LINE SHOWN IN PHOTOGRAPH, STAGE 5, E.M. GRID, AUTOMOBILE EXHAUST

TABLE 3. RELATIVE CONCENTRATIONS OF ELEMENTS DETECTED IN ATMOSPHERIC SAMPLES

H = high, M = medium, L = low, T = trace, ND = not detected.

Sample Descprition	Element														
	Pb	Cl	Br	Al	Zn	Fe	Mn	S	P	Si[a]	Ca	Cu	K	Ng	Mg
Stage 4, Be disk, random area	L	T	T	T	L	H	M	L	ND	H	T	T	L	ND	ND
Stage 4, Be disk, high iron	T	ND	ND	ND	T	H	M	M	ND	L	T	T	M	ND	ND
Stage 4, Be disk, high zinc	ND	L	ND	ND	H	M	L	L	ND	L	ND	ND	L	ND	ND
Stage 4, Be disk, high lead	H	H	H	L	ND	M	ND	H	T	H	T	T	H	ND	ND
Stage 4, Be disk,[b] high calcium	ND	T	ND	L	L	M	T	H	ND	H	H	L	L	ND	L
Stage 5, Be disk, random area	L	ND	ND	T	ND	T	T	M	ND	H	ND	ND	L	ND	ND
Stage 5, Be disk, high sulfur	L	ND	ND	ND	ND	T	ND	H	ND	M	T	ND	ND	ND	ND
Stage 5, Be disk,[c] high iron	ND	ND	ND	M	ND	H	ND	H	T	H	T	ND	M	ND	ND
Stage 5, Be disk, high lead	H	M	H	ND	T	T	ND	M	L	H	T	ND	L	ND	ND
Stage 2, Be disk,[d] high copper	ND	M	ND	H	ND	T	ND	M	ND	H	T	H	ND	ND	ND
Stage 2, Be disk,[e] high titanium	ND	ND	ND	ND	ND	T	ND	ND	ND	H	T	ND	ND	ND	ND
Stage 2, Be disk,[f] high lead	H	L	L	H	ND	H	L	L	T	H	T	ND	L	T	T
Stage 2, Be disk, high sodium	ND	ND	ND	ND	ND	ND	ND	L	ND	L	ND	ND	L	H	L
Stage 2, Be disk, high iron	ND	ND	ND	ND	L	H	ND	M	ND	H	T	ND	ND	ND	ND
Stage 2, Be disk,[g] high calcium	ND	T	ND	T	ND	T	ND	L	ND	H	H	ND	T	ND	T
Stage 3, Be disk, high iron	ND	ND	ND	ND	ND	H	L[h]	L	ND	H	T	ND	T	ND	ND
Stage 3, Be disk, high calcium	ND	ND	ND	L	T	T	T	T	ND	M	H	ND	ND	ND	T
Stage 3, Be disk, high zinc	ND	T	ND	ND	H	ND	ND	T	ND	M	ND	ND	T	ND	ND
Stage 3, Be disk high lead	H	T	M	L	ND	L	T	T	ND	L	L	ND	L	ND	ND
Stage 3, Be disk, high sulfur	ND	ND	ND	L	ND	ND	ND	H	ND	M	ND	ND	L	L	ND
Stage 3, Be disk, high aluminum	ND	ND	ND	H	ND	H	ND	T	ND	H	T	ND	M	ND	T

(a) Silicon is present in trace amounts from the silicone grease used to coat the beryllium disks; however, readings in the table take this into account.
(b) Tin, titanium and chromium were found in trace amounts in this particle.
(c) All high iron particles in this sample show medium potassium and aluminum.
(d) Particles show nickel (low).
(e) Unusual particle, probably TiO_2.
(f) Many high lead particles were found with various compositions. All lead particles found have bromine and chlorine associated with them.
(g) Particle had titanium.
(h) Not all particles show Mn.

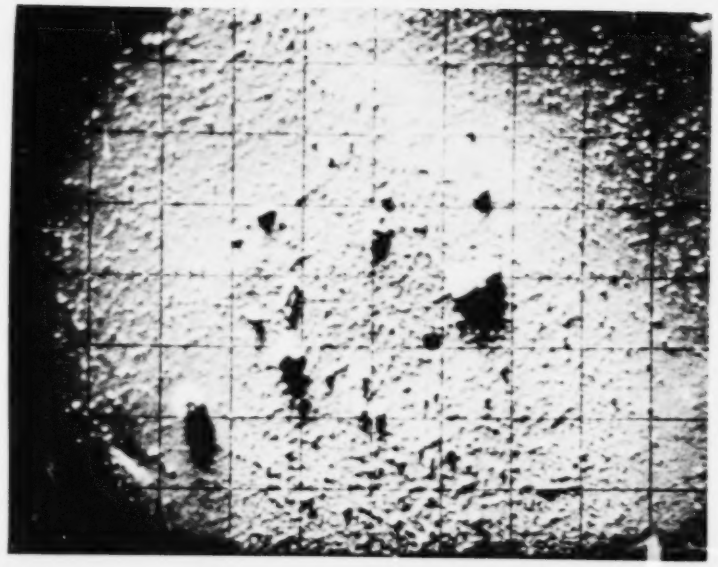


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FIGURE 21. B.S.E. IMAGE STAGE 4, Be DISK, ATMOSPHERIC SAMPLE

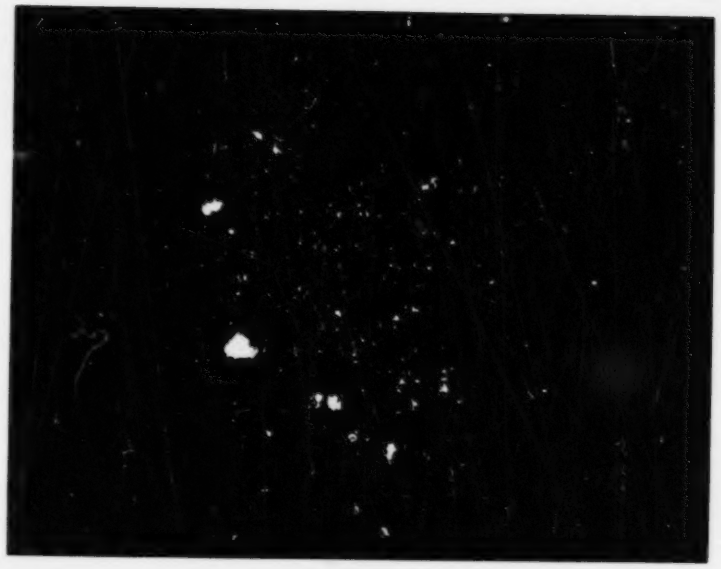

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FIGURE 22. Pb DISTRIBUTION IN AREA SHOWN IN FIGURE 20

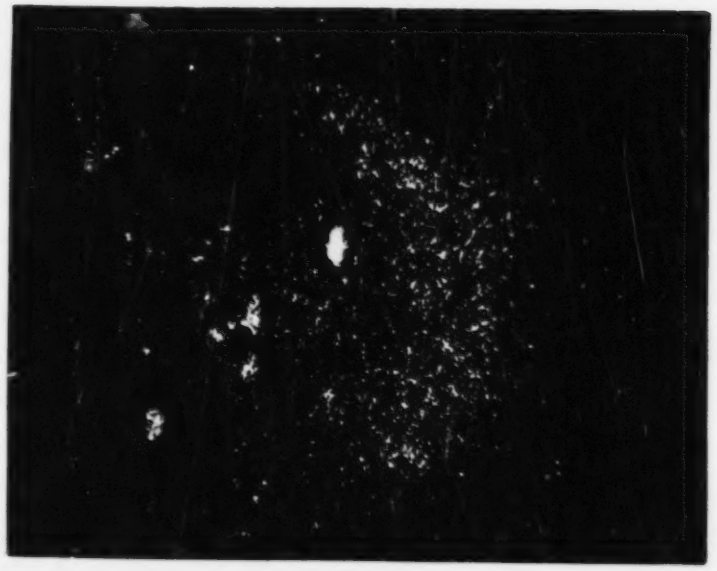

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FIGURE 23. Si DISTRIBUTION IN AREA SHOWN IN FIGURE 20

150X

FIGURE 24. Br DISTRIBUTION IN AREA SHOWN IN FIGURE 20

150X

FIGURE 25. Zn DISTRIBUTION IN AREA SHOWN IN FIGURE 20

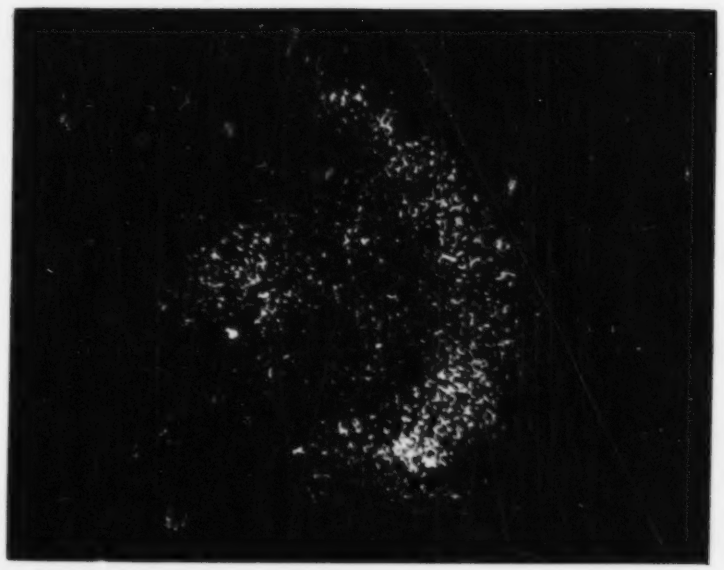

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FIGURE 26. Fe DISTRIBUTION IN AREA SHOWN IN FIGURE 20

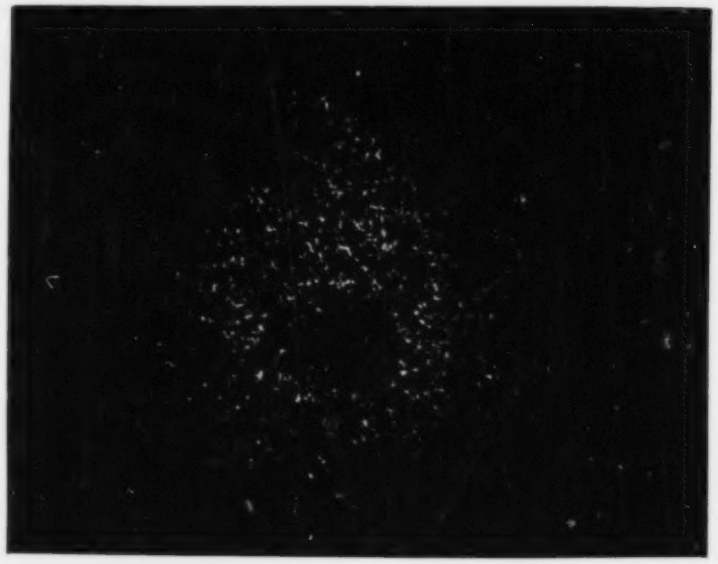

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FIGURE 27. Mn DISTRIBUTION IN AREA SHOWN IN FIGURE 20

150X

FIGURE 28. Ca DISTRIBUTION IN AREA SHOWN IN FIGURE 20

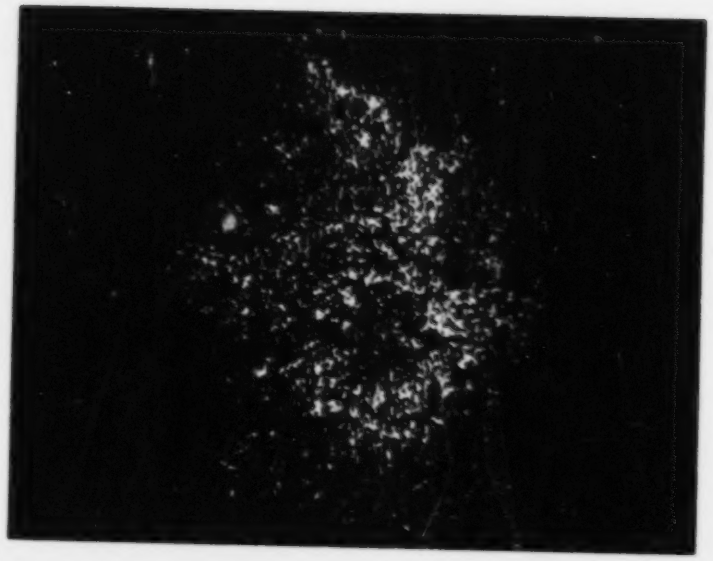

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FIGURE 29. S DISTRIBUTION IN AREA SHOWN IN FIGURE 20

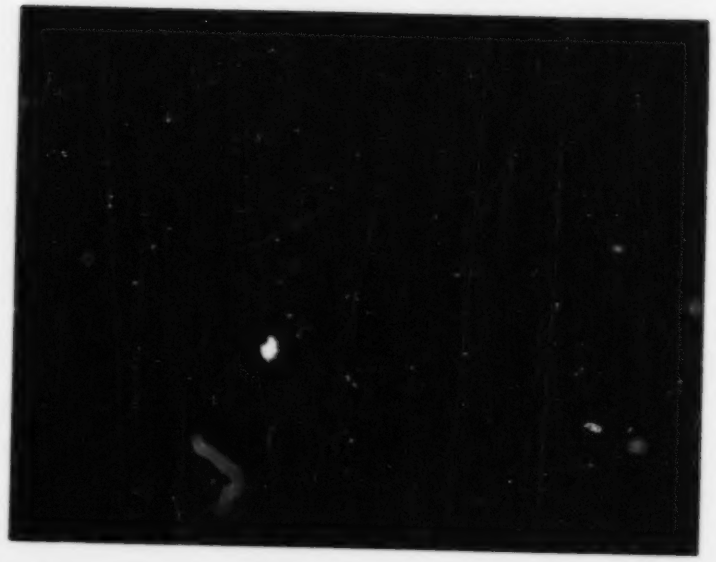

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FIGURE 30. Cl DISTRIBUTION IN AREA SHOWN IN FIGURE 20

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FIGURE 31. K DISTRIBUTION IN AREA SHOWN IN FIGURE 20

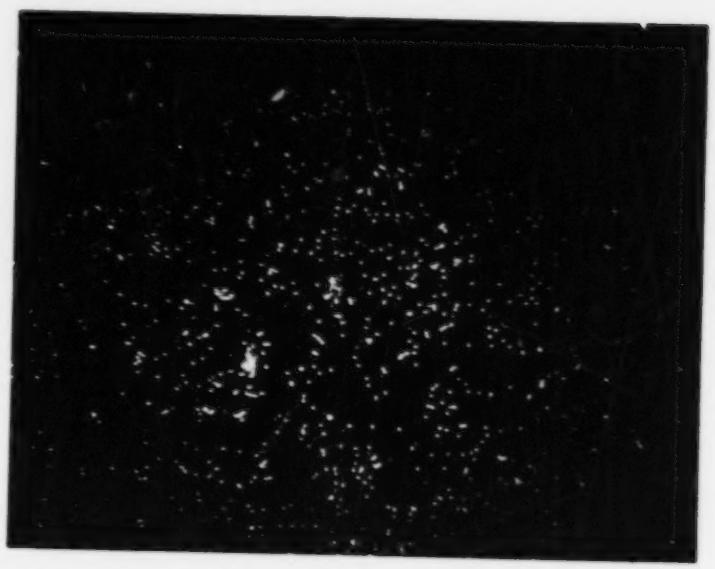

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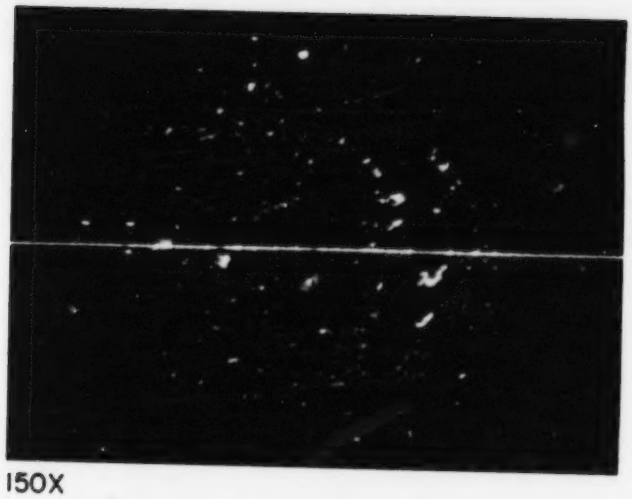
FIGURE 32. Al DISTRIBUTION IN AREA SHOWN IN FIGURE 20



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B.S.E. Image Showing Scan Line

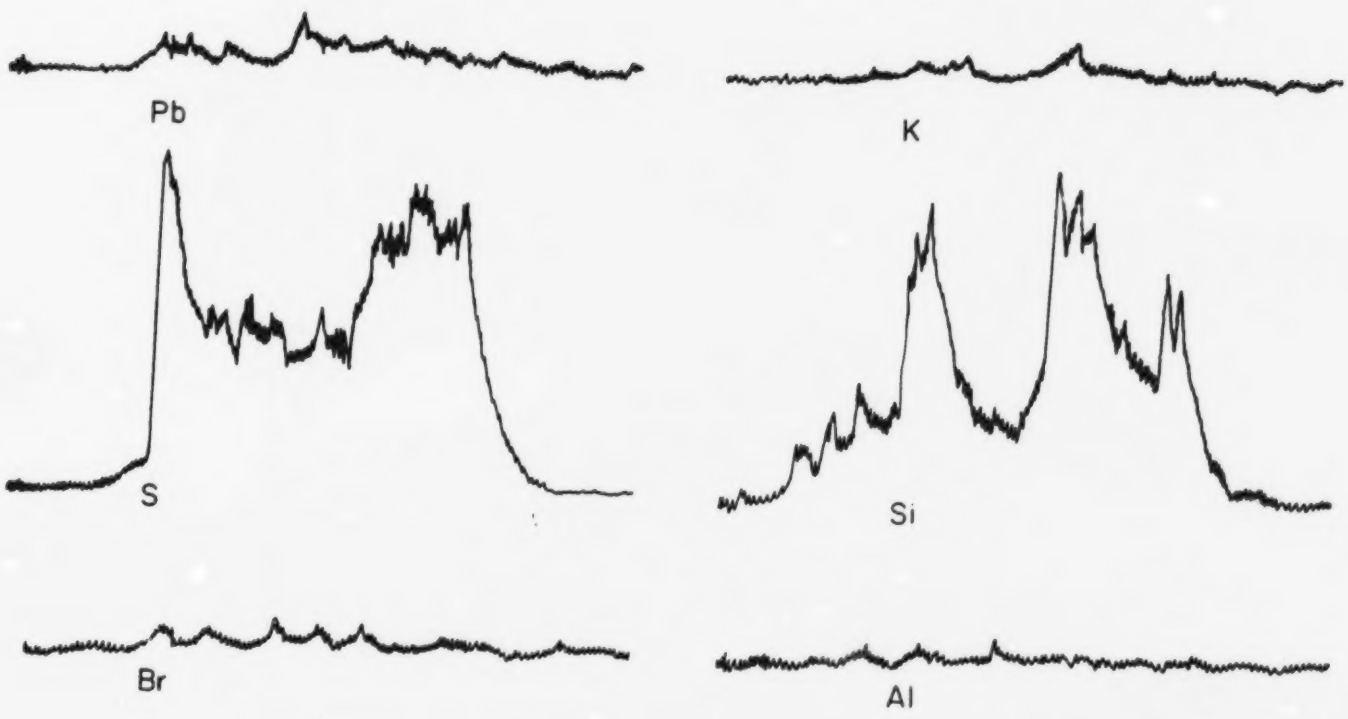

FIGURE 33. X-RAY SCANS ALONG LINE SHOWN IN PHTOGRAPH, STAGE 5, Be DISK, ATMOSPHERIC SAMPLE

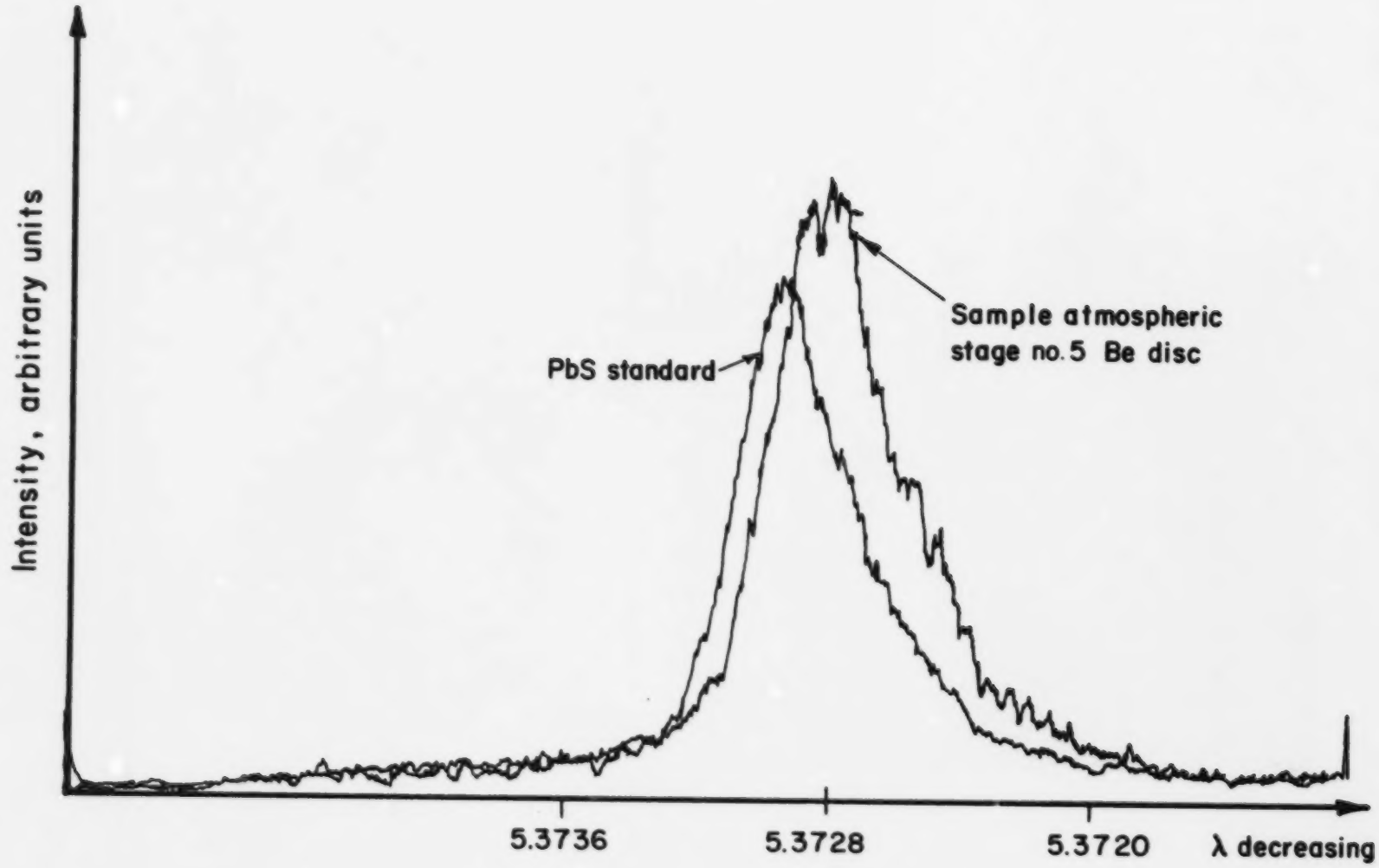

FIGURE 34. ELECTRON MICROPROBE ANALYSIS OF ATMOSPHERIC SAMPLE – SULFUR WAVELENGTH SHIFT

A BSE image of the deposit was obtained (Figure 33) and individual line scans for Pb, K, Si, Si, Br, and Al were made along the line visible in the photograph.

A BSE image and X-ray distribution photos were obtained for this sample; however, since they are basically similar to those already presented for the Stage 4 sample, they are not included in this report.

Individual particles with high specific-element content were located and wavelength scans for several of these particles are summarized in Table 3. Particles run include high sulfur, high iron, and high lead. BSE image and X-ray distribution photos were obtained for each of the particles examined. As in the previous samples, particles having a high lead content also contain bromine and chlorine.

A sulfur-wavelength-shift measurement was made (Figure 33), similar to that run for the automobile exhaust sample (Figure 19). Figure 34 shows the sulfur spectrum from the sample compared with the spectrum from PbS. As in the case of the automobile exhaust, the majority of the sulfur present in the sample is in the sulfate form. The double peak again might indicate the presence of elemental sulfur, but this would have to be confirmed by additional measurements.

Atmospheric Samples, Stage 2, Beryllium Disk. The sample density was lower on this sample than any previous samples, but many large individual particles were found scattered over a large area. Since the deposit was so widely and thinly dispersed on the beryllium disk, a random-area wavelength scan was not made. A BSE image (Figure 35) was obtained as well as X-ray distribution photographs for Ca, Ti, Fe, Ca, Zn, Pb, Br, Al, Si, S, Cl, K, and Mg. The X-ray distribution photos are not included in this report, since they are similar to those already shown for the Stage 4 sample. The chart scans obtained for this sample confirmed the presence of many individual large particles.

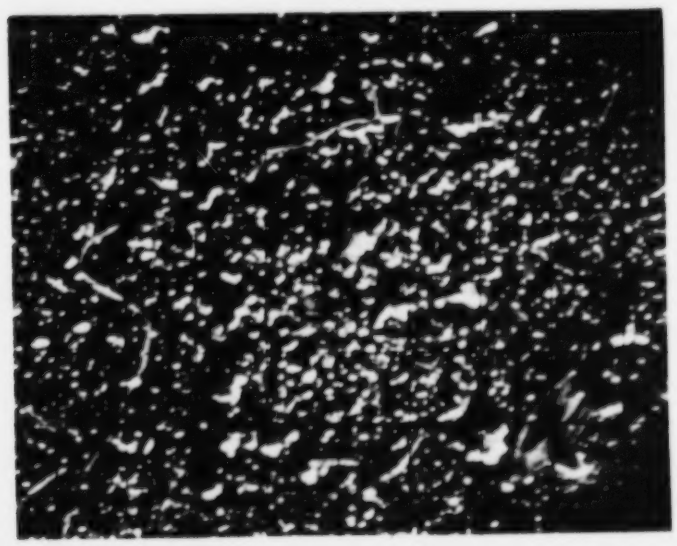

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FIGURE 35. BSE IMAGE SHOWING SAMPLE DEPOSIT, STAGE 2, Be DISK, ATMOSPHERIC SAMPLE

Wavelength scans for particles high in specific elements were obtained, with the results summarized in Table 3. Particles run include high copper, high titanium, high lead, high sodium, high iron, and high calcium.

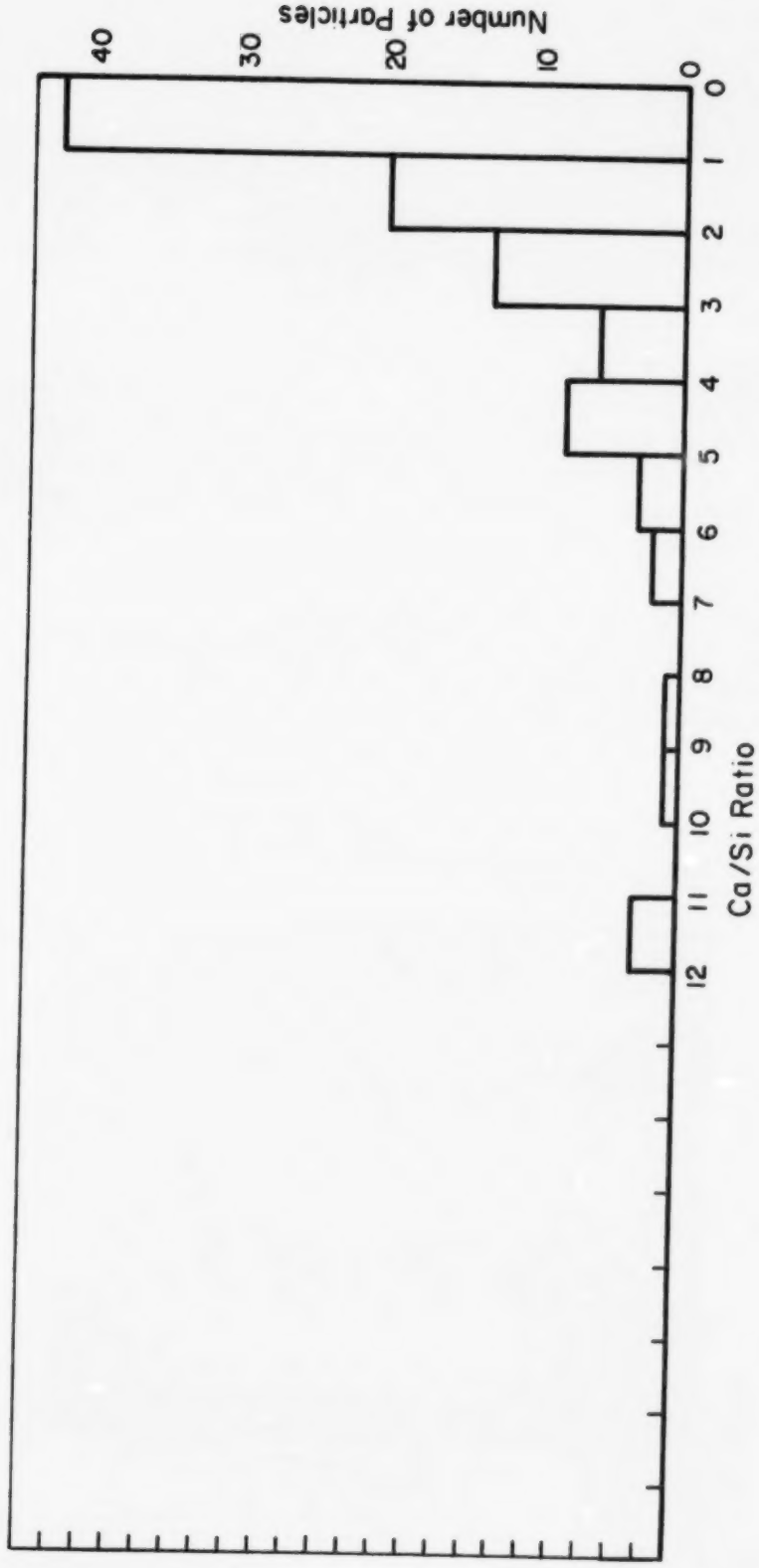


FIGURE 36. FREQUENCY OF INTENSITY RATIOS FOR CALCIUM-SILICON (100 PARTICLES MEASURED)

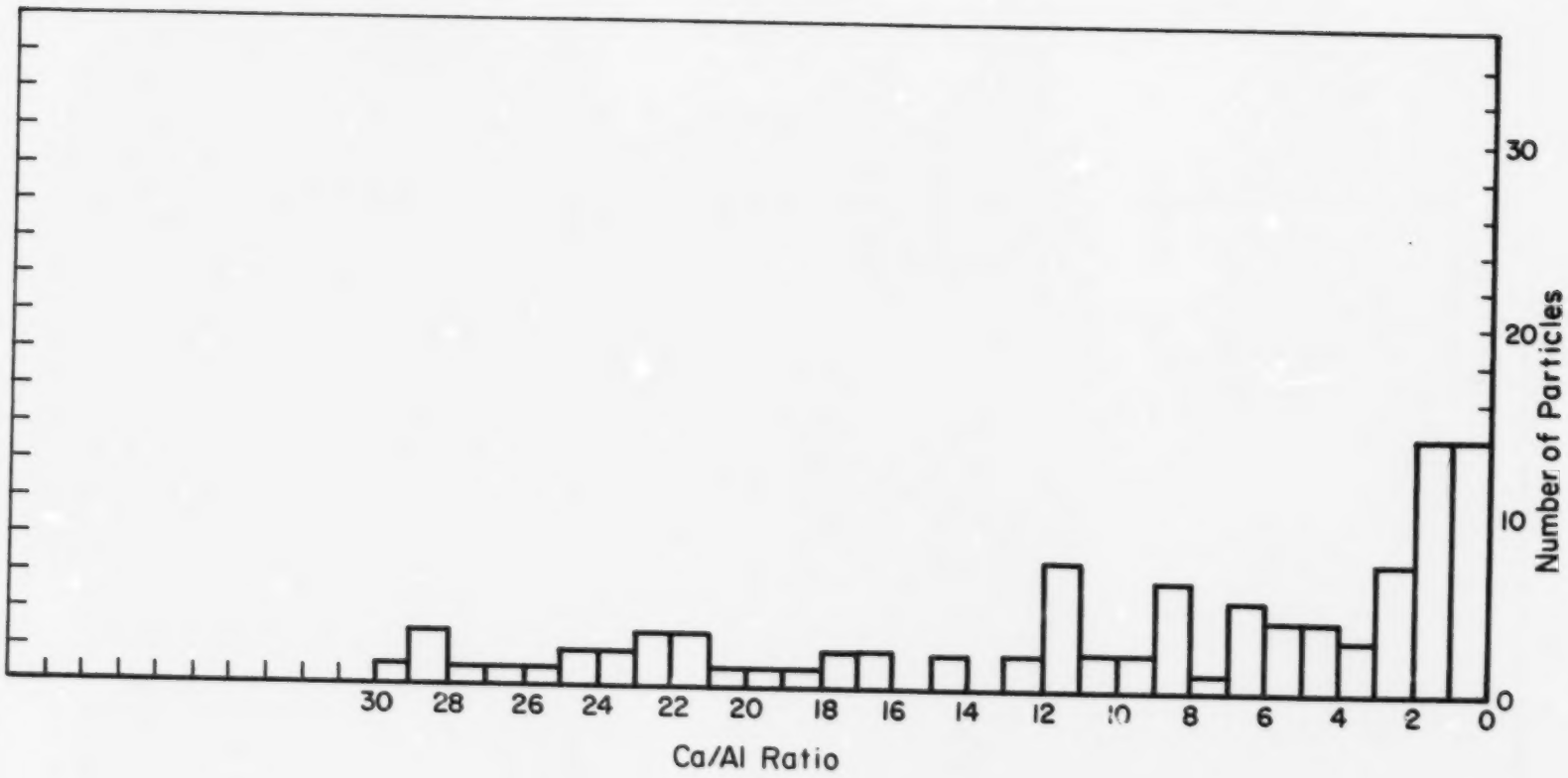


FIGURE 37. FREQUENCY OF INTENSITY RATIOS FOR CALCIUM-ALUMINUM (100 PARTICLES MEASURED)

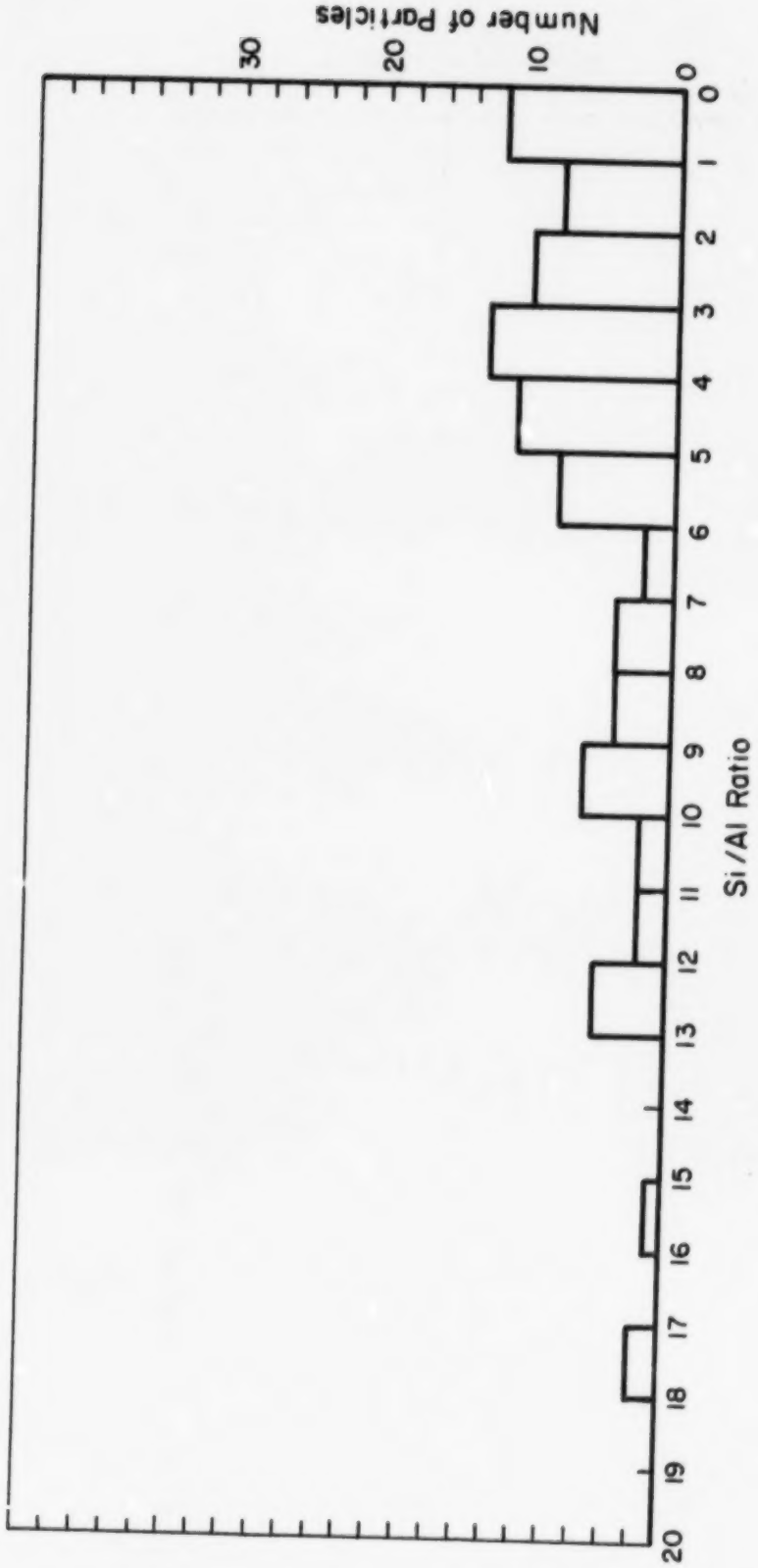


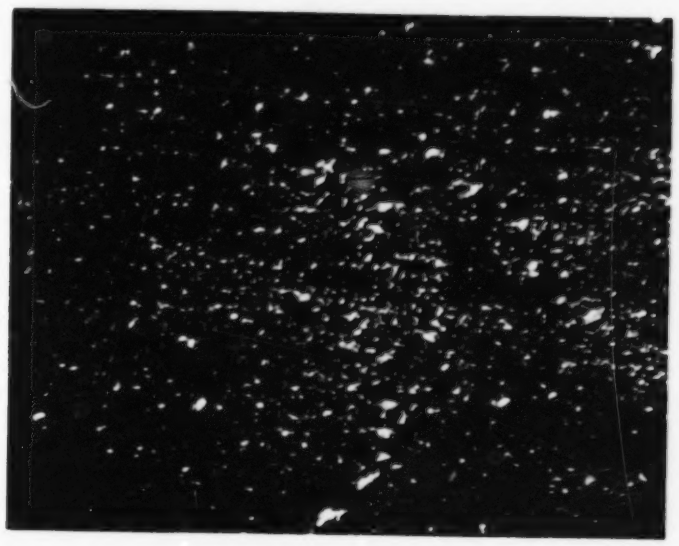
FIGURE 38. FREQUENCY OF INTENSITY RATIOS FOR SILICON-ALUMINUM (100 PARTICLES MEASURED)

For this sample, it was decided to see if there were many particles with similar elemental compositions or if the compositions varied greatly from particle to particle. Consequently, the method of White, Denny, and Irving[1] was used to analyze 100 of the calcium-containing particles. This method recognizes that for small particles, the particle-to-particle variation in absolute X-ray intensities for a given element may vary by over an order of magnitude, depending on the fraction of the incident electron beam absorbed by the particle. They found that the intensity ratio for two elements is essentially independent of particle size and shape in a mixture of particles of the same composition. Thus, by measuring intensity ratios and plotting against known composition, one can determine quite accurately the composition of unknown particles.

The procedure followed in making the ratio measurement was to select a particle from the X-ray image; then the electron beam was positioned directly on the particle and both elements were counted simultaneously for 10 seconds. Duplicate intensity readings were made for each particle. There is a very definite advantage in the simultaneous measurement of the two elements, since an error in beam positioning is cancelled out as are errors in resetting the spectrometers. Of course, there is a corresponding savings in time for each analysis.

Figure 36 is a graph showing the relative frequency of intensity ratios for Ca/Si on 100 measured calcium-containing particles in this sample. Figure 37 is a similar graph showing the Ca/Al intensity ratio, while Figure 38 shows the Si/Al ratio. The wide variations in intensity ratios is apparent from these figures, and we can thus conclude that there is a wide variation in the composition of individual particles. Extensive statistical analysis involving several thousand particles would be necessary to make more definite statements. For this type of analysis, a probe with automated readout is nearly a necessity, as operator time becomes excessive.

Atmospheric Samples, Stage 3, Beryllium Disk. The particle density of this sample was greater than that of the previous sample, and individual particle could easily be seen. Figure 39 is a BSE image of this sample showing the particle distribution.



150X

FIGURE 39. BSE IMAGE SHOWING SAMPLE DEPOSIT, STAGE 3, Be DISK, ATMOSPHERIC SAMPLE

X-ray distribution pictures were also taken for Ca, Si, Al, S, Cl, Fe, K, Pb, Br, and Mg, but these again are similar to those previously presented and are not included in this report.

Wavelength scans for particles high in specific elements were obtained, with the results shown in Table 3. Particles run include high iron, high calcium, high zinc, high lead, high sulfur, and high aluminum.

Evaluation of Experimental Data

When the rough data regarding particles containing high lead in the automobile-exhaust samples and in the atmospheric samples are tabulated, it is easy to see the correlation of the lead with chlorine and bromine (see Table 4). Study of this table points the way for an interesting set of experiments on the lead-chlorine-bromine relationship in atmospheric samples. Intensity ratios for these elements should be measured in many particles; the results should prove a definite correlation. It is unfortunate that under the scope of this program this could not be done; however, since the qualitative relationship has been demonstrated, the quantitative measurement should be a routine matter. If the chlorine and bromine are examined in Table 4, it can be seen that there is an increase in the relative amounts from Stage 2 to Stage 5 (Stage 2 trapping the larger particles and Stage 5 the smallest). The lead concentrations for these stages are simply listed as "high", since at the scale factors used to detect the other elements, the lead was off scale in all cases. Closer investigation has shown that the concentration of lead in the individual particles increases as the particle size decreases and that there is a definite corresponding correlation for the chlorine and bromine values. Distributions on the cascade impactor stages for several other elements seem highly dependent on the particle size, specifically iron, aluminum, and manganese, which decrease with particle size. Specifically, it seems that the high-lead-content particles located on Stage 5 of the cascade impactor have higher lead, chlorine, and bromine than those from the other stages (larger particle size). The larger particles contain higher quantities of Al, Fe, and Mn. Thus, there seems to be a definite separation of the elements by particle size.

TABLE 4. RELATIVE CONCENTRATIONS OF ELEMENTS DETECTED IN PARTICLES OF HIGH LEAD CONTENT FOR AUTOMOBILE EXHAUST AND ATMOSPHERIC SAMPLES

Data Condensed From Tables 1 and 3.

Sample Description	Element											
	Pb	Cl	Br	Al	Zn	Fe	Mn	S	P	Si	Ca	K
Stage 4, Be disk, auto exhaust	H	H	H	ND	T	L	ND	T	T	H	L	ND
Stage 2, Be disk, atmospheric	H	L	L	H	ND	H	L	L	T	H	T	L
Stage 3, Be disk, atmospheric	H	T	M	L	ND	L	T	T	ND	L	L	L
Stage 4, Be disk, atmospheric	H	H	H	L	ND	M	ND	H	T	H	T	H
Stage 5, Be disk, atmospheric	H	M	H	ND	T	T	ND	M	L	H	T	L

H = high, M = medium, L = low, T = trace, ND = not detected.

Energy Dispersive Analysis

In order to test the relative sensitivity of energy-dispersive and crystal-dispersive systems, a Nuclear Diodes lithium-drifted silicon semiconductor detector was fitted to a Cambridge Scanning Electron Microscope.

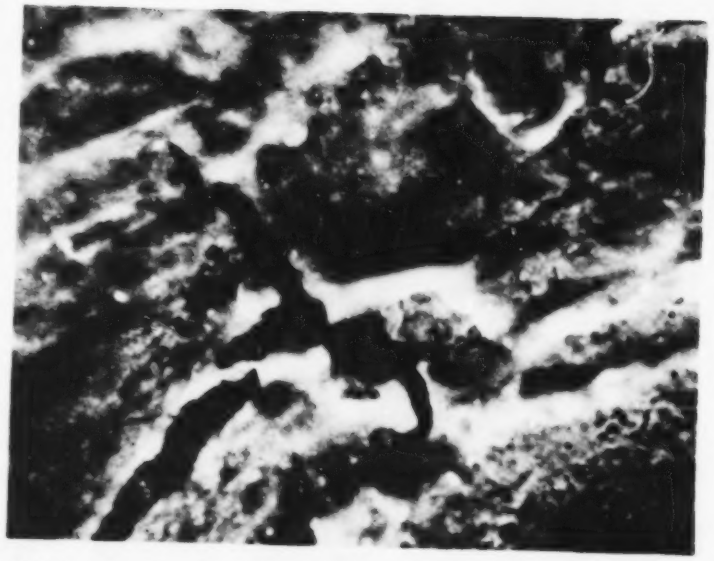
Since a scanning electron microscope (SEM) is quite similar in principle to the microprobe, it is quite easily adapted for energy-dispersive analysis.

The normal-wavelength dispersive spectrometer such as is used in the microprobe analyzes X-rays by diffracting them off a crystal and observing the angle (wavelength) where the Bragg equation is satisfied ($N\lambda = 2d \sin \theta$). This type of detection is capable of X-ray resolution of a few electron volts, hence it is no problem to separate the wavelengths of adjacent elements. The wavelength dispersive spectrometer is, however, a very low-efficiency device, and it has the disadvantage of being a "single channel" device in that it can examine only one wavelength at a given time. Also, at the very low beam currents used in a SEM, the intensity of X-rays produced is very much less than is that produced in a microprobe, and, also, very long analysis times are necessary.

An energy-dispersive spectrometer has the advantage of recording, essentially simultaneously, the full spectrum of the X-rays present. This detector gives a signal that is proportional to the energy of the X-ray photons and, thus, the X-ray spectrum is dispersed according to its energy. This type of detector is very efficient, since it can be placed close to the sample and can view a significant solid angle. Furthermore, since the entire spectrum can be viewed and recorded in a very few seconds, the total analysis time is generally short. The major fault associated with energy-dispersive devices is their lack of resolution (about 200 ev), which is considerably poorer than the crystal spectrometer. In many cases, however, this resolution is sufficient for practical detection of elements from about oxygen and higher in the periodic table.

The Stage 5 automobile exhaust sample collected on an electron microscope grid was mounted and placed in the SEM. Since the electron microprobe had previously detected particles with high concentrations of calcium in this sample, the pulse height analyzers of the Nuclear Diode analyzer was set to accept only the calcium peak, and a scan at 1000X was made over several areas of the sample. The SEM can be modified to produce X-ray pulse pictures similar to those obtained on the microprobe, and by this method an area was located that seemed to have a particle with calcium concentrated in it. Figure 40 is a high-resolution, back scattered electron image of the selected area, while Figure 41 is the X-ray distribution for calcium obtained on the SEM. Figure 42 shows a BSE image of the same area taken on the electron microprobe; the superior resolution of the SEM photograph (Figure 40) is evident. Figure 43 is the X-ray distribution for calcium obtained in the microprobe, and, in this case, it is easy to see the superior X-ray peak-to-background resolution of the microprobe when compared with the SEM X-ray distribution (Figure 41).

The electron beam of the SEM was positioned on the particle showing the high calcium, and the spectrum was recorded by the energy-dispersive spectrometer (Figure 44). Elements that can positively be identified from this spectrum are Cu (from the electron microscope grid), Al, Cl, Ca, Pb, and Br.



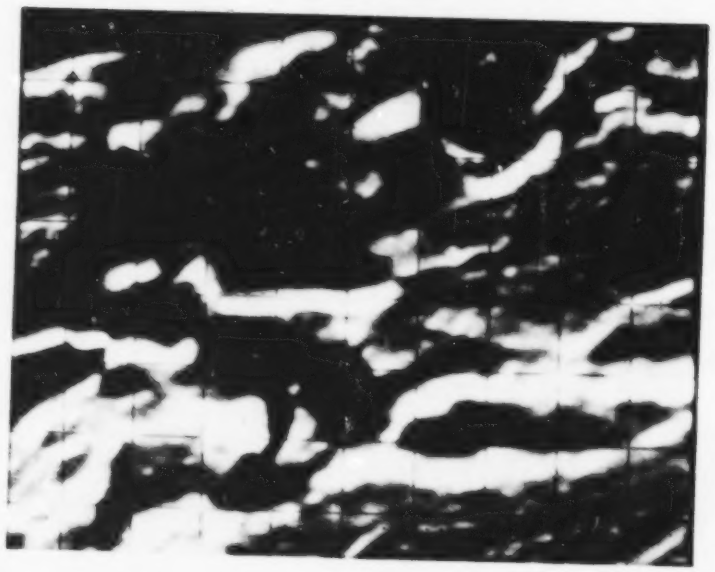
1000X

FIGURE 40. SCANNING ELECTRON MICROGRAPH OF AREA FROM STAGE 5, AUTO EXHAUST, E. M. GRID

1000X

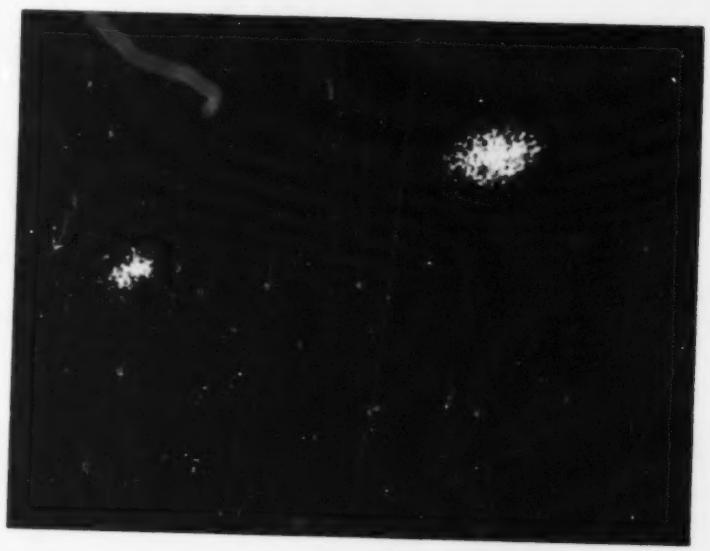
FIGURE 41. X-RAY DISTRIBUTION FOR Ca IN SAME AREA AS FIGURE 39

Energy Dispersive Spectrometer Mounted on S. E. M.



1000X

FIGURE 42. B. S. E. IMAGE OF SAME AREA AS FIGURE 39 TAKEN ON ELECTRON MICROPROBE



1000X

FIGURE 43. X-RAY DISTRIBUTION FOR Ca IN SAME AREA AS FIGURES 39 AND 41

Electron Microprove Wavelength Dispersive Spectrometer

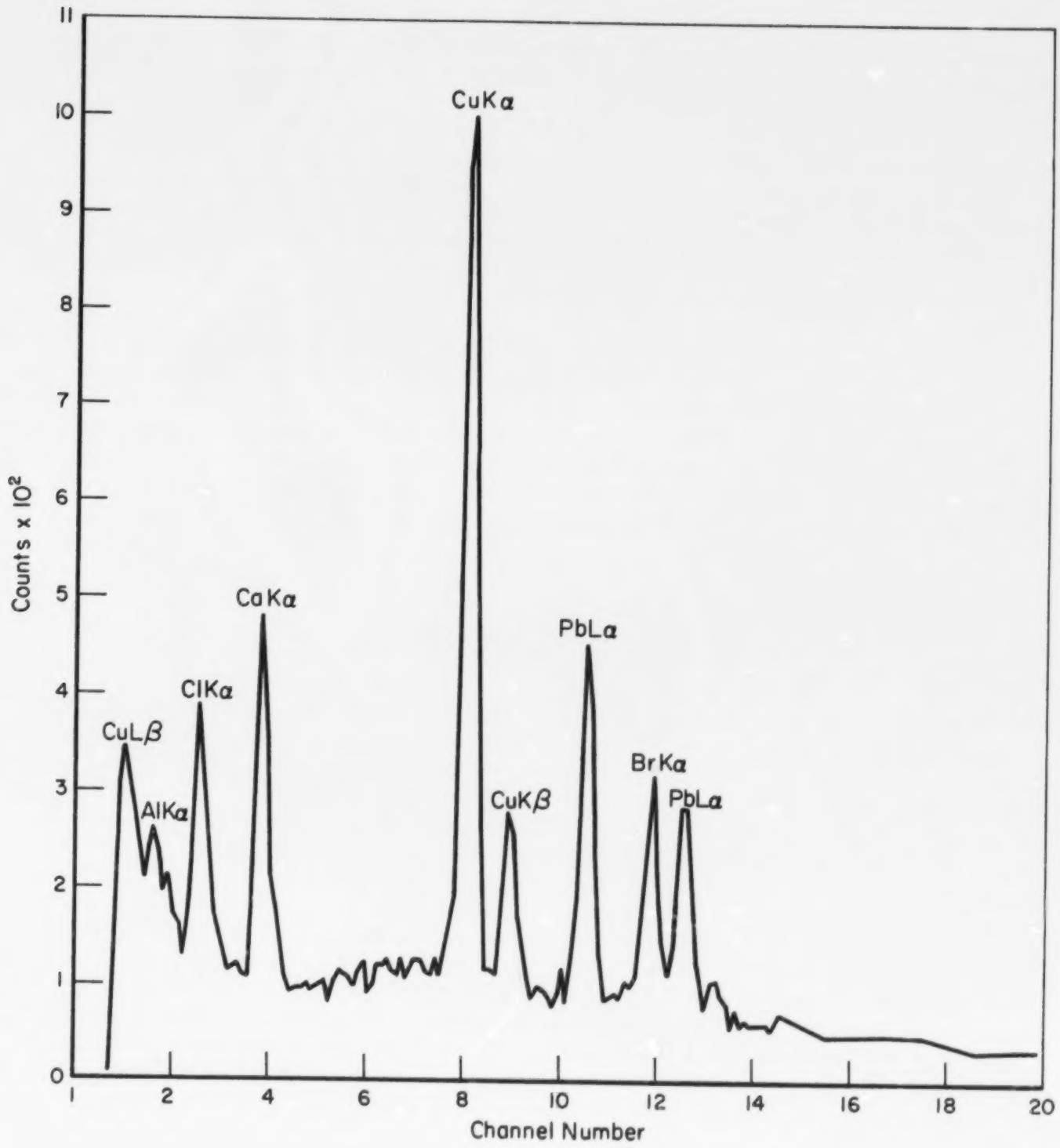


FIGURE 44. SPECTRUM OBTAINED BY ENERGY-DISPERSIVE SPECTROMETER, STAGE 5, AUTOMOBILE EXHAUST, E. M. GRID, HIGH CALCIUM PARTICLE

This same particle was run in the electron microprobe, and the same elements were found (considerably higher peak-to-background ratio), as well as Si, S, Zn, and Fe.

In this case, the energy dispersion gave a spectrum of the major elements in about 36 seconds, compared with about 55 minutes for the wavelength scan on the microprobe. It did not detect a few elements that were found in trace amounts by the microprobe.

The question must be asked, "Just what information is desired in particle analysis?" If one were seeking only the major components of many particles, then the energy-dispersive system is clearly superior. On the other hand, if one is interested in trace components in particles containing a specific element, then the wavelength spectrometer is superior because the wavelength spectrometer can be set to a specific element and can find a particle containing that element just as fast and with greater sensitivity than the energy-dispersive spectrometer.

In this particular example, if sulfur had been present in more than trace amounts, it would have interfered with the chlorine peak, and the energy-dispersive spectrometer could not have separated the true peaks. The same is true of the silicon-aluminum pair. Perhaps a computer could smooth out the curves, but the time element for analysis then becomes important. The wavelength dispersive spectrometer has no difficulty in separating these adjacent-element peaks and also has the advantage of providing quantitative data if desired. The energy-dispersive system is semiquantitative at best.

CONCLUSIONS

The efforts on this program demonstrate clearly that the electron microprobe analyzer is a useful and proper instrument for the examination of air pollution particulate matter. The present limitations are not so much that of the instrument but rather the type and method of specimen collection. During this project, it became apparent that, given a suitable sample, a great deal of information can be obtained on particles down to about 0.1 μ in diameter. At the present state of the art, particles smaller than this cannot be examined because the X-ray count ratios are too low, and the particles are almost invisible on the electron-scanning image and are not visible at all on the light optical system. It seems clear that the minimum size of particle permitting accurate quantitative analysis lies between 1 and 5 microns. It is possible to obtain information on the composition of smaller particles, but such information is generally qualitative at best, especially in the situation where X-rays may be excited simultaneously from the particle and a substrate material; once the characteristic radiation from the particle is overwhelmed by the background radiation from the substrate, even qualitative analysis of particles much smaller than 0.5 μ is impossible.

If the specimen collecting conditions are directed to producing dispersed particles on a substrate producing no X-ray background (such as beryllium or carbon films), interference from the substrate is avoided and particles much smaller than 1 micron can be analyzed qualitatively with a fair degree of certainty. If two or more elements are present, some degree of quantification is possible using the ratio method described previously.

The importance of using the electron microprobe in conjunction with other analysis techniques cannot be overemphasized. Use of electron microprobe analysis, complemented by scanning electron microscopy, X-ray diffraction, electron microscopy, optical microscopy, mass spectrometry, and chemical analysis becomes a powerful system for characterizing particles. The practical usefulness of combining these techniques is particularly evident in a laboratory where all of the instruments are available and there is constant and close cooperation among those responsible for using the various methods.

The question as to which instrument is best suited for particle analysis has no real answer; it all depends on what information is desired. The scanning electron microscope is indispensable if surface-morphology information is desired; no present commercial microprobe can supply the necessary resolution to provide surface detail on 0.1-μ particles. The compromises necessary to provide this resolution detract from the X-ray and/or light optical performance of the basic microprobe instrument. If the problem is to detect one particle in several thousand with a specific elemental composition, an automated microprobe may best fit the requirements. If a fast general analysis of the major elements in many particles is desired, energy-dispersive analysis on a scanning electron microscope or conventional electron microprobe is probably more suitable.

Ideally, one should have at least three separate instruments – the electron microprobe, the scanning electron microscope, and the transmission electron microscope, with techniques developed so that the specimens can be interchanged easily between these instruments and the same area and/or particle easily located. This is not as difficult as it may sound, and only by a combination of these techniques can the maximum amount of information be obtained about a particle or particles.

In commercial instrumentation, the electron microprobes currently available do provide much better scanning facilities than those available just a few years ago, but this scanning facility is approaching the limit that can be expected without degrading X-ray performance. Instruments incorporating microanalysis and transmission electron microscopy have been built, but at this time are not commercially available in a useful form. Energy-dispersive systems should be watched closely, as improvements in this field have been very rapid, and, if the sample is designed around the peculiar limitations of the energy-dispersive system, a lot of useful information may be obtained in a very short time.

In general, at the present state of the art, the most valuable single instrument commercially available would be an automated, programmable scanning electron microprobe with both wavelength and energy-dispersive spectrometers. Such an instrument is available from several manufacturers at about $125,000 to $150,000. If some compromises are made, an adequate instrument for many applications of particle analysis could be purchased for about $60,000 to $80,000.

RECOMMENDATIONS FOR FUTURE WORK

It must be emphasized that present methods of collecting air pollution particles are not adequate to provide the maximum amount of information from single particles, and an experimental program to develop suitable techniques is necessary. For example, it is often easier to disperse particles from a liquid medium; collection techniques involving electrostatic precipitation into a liquid media should be investigated. There are also many transmission electron microscopy techniques that are applicable to microprobe analysis and which could be easily utilized.

The aspect of suitably moving specimens from instrument to instrument, yet keeping track of individual particles, has been mentioned. This technique development is necessary to provide the maximum information from small particles.

An investigation of the lead-chlorine-bromine correlation in atmospheric and automobile exhaust samples by the use of intensity ratio techniques would provide very useful information and should be undertaken as a separate program.

APPENDIX

GENERAL OUTLINE OF THE ELECTRON MICROPROBE POTENTIAL AND APPLICATIONS TO AIR POLLUTION RESEARCH

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GENERAL OUTLINE OF THE ELECTRON MICROPROBE POTENTIAL AND APPLICATIONS TO AIR POLLUTION RESEARCH

The utility of the electron microprobe method in the chemical analysis of micron-size volumes is well known. The fields of study to which the method has been used encompass metallurgy, ceramics, geology, biology, electronics, and others. To date, most applications have been predominantly concerned with the in-situ analysis of microscopic regions in solid materials where the specimen is essentially of infinite size compared with that of the electron-bombarded region. Very limited applications involving the analysis of individual particles in the micron-size range have also been carried out.

One type of application to which the microprobe method has not been extensively extended but from which very useful chemical information can be derived is the analysis of particles of microscopic dimensions. The complexity – and hence the practical realization – of such an application is critically dependent on the characteristics of the particles and the information desired. The principal factors determining this complexity include the following:

- Specimen collection and preparation requirements
- The size range of the particle of interest
- The number of elements requiring analysis
- The total number of particles requiring analysis
- The maximum number of particles which can be analyzed simultaneously
- The need for correlating X-ray data with individual particles
- The volume and element analysis resolution required
- The degree of accuracy required in the chemical analysis.

Thus, in view of the variability to which these factors would be restrictive for a given problem, a method by which particle analysis could be carried out cannot be stated in a simple manner. An understanding of the restrictive nature of each of these factors is necessary to determine the procedures required to obtain the maximum amount of information from a given situation.

This section is directed to the extension of the microprobe method to the specific application of particle analysis. The procedures and instrumentation required for this purpose are discussed. In so doing, the limitations of the microprobe method – in terms of the basic physics of the technique as well as instrument restraints – are cited.

In spite of all the work being carried out related to air pollution, very little is known about the composition and fine structure of the individual airborne particles that

seem to present major problems. This is especially true of the particles in the size range from about 1 micron and below where classical methods of identification such as chemical analysis, light microscopy, electron microscopy, and X-ray diffraction are severely limited. Considering the possible high rate of reactivity because of high specific surface area and the degree of pulmonary retention of this size particles, it seems imperative that their characterization be attempted. This information is desirable, not only from the basic aspect of identification but also to relate atmospheric particulates with specific source effluents, to understand more fully the basic aerosol mechanisms, and to assess the effects on materials, animals, and humans.

One of the most powerful tools for single-particle identification is the electron microprobe analyzer. In this device small areas from a few tenths of a micron to several hundred microns can be examined nondestructively in several different modes to establish the spatial distribution and the identification of any element from atomic number 5 (boron) through 92 (uranium). Simultaneous with elemental identification, the topography of a sample can be photographed to help relate the probe information to light or scanning electron microscopy examinations. Most elements can be detected in a homogeneous sample at levels as low as 100 ppm, while isolated particles of an element can be identified if as little as 1×10^{-15} grams is present in a small area.

There are many problems associated with the analysis of particles below 1 micron in size in the electron microprobe analyzer. First and foremost is the fact that most commercial microprobes have a beam size (and thus imaging resolution) on the order of 1 micron, making imaging by the conventional techniques of back-scattered electron or specimen current images of little value. The problem, of course, is that if the particle cannot be found by the light microscope incorporated in the analyzer or by one of the conventional scanning modes, it is impossible to determine in advance where a particle of interest is located. Even though the X-ray system may be sensitive to as little as 1×10^{-15} gram, it may be impossible to locate and analyze a particle with sufficient mass using conventional techniques.

It is generally agreed that there is little problem in the qualitative and quantitative analysis of particles down to a size range of 2 to 5 microns, depending on their density and conductivity. Below this size, the X-ray intensity falls off, though smaller samples can be analyzed by ratios or by a known size correction. Nonconductive particles present problems of their own because of defocusing and deflection of the electron beam due to the charge buildup on the particle. This effect often can be minimized by coating the particles with a thin layer of carbon or other suitable material.

The qualitative and quantitative determinations with an electron microprobe depend upon the quality and versatility of the visual optical system, the resolution and efficiency of the electron optics, and the detection capability of the X-ray spectrometers. Essentially all electron microprobes available today can be expected to provide about the same quality of information about a particulate sample. Some microprobes are more versatile than others and some have special additional features that make them attractive; however, at present, all have virtually the same electron-imaging resolving power and X-ray sensitivity. The successful examination of particles of 1 micron in size and below presently is limited by the characteristics of the current electron microprobes and the experience and skill of the operator.

The ability to obtain specific chemical information on small particles with the electron microprobe is strongly dependent on certain physical limits. These limits are

somewhat variable but are basically determined by instrument design and specimen characteristics as well as basic theoretical considerations. In any practical situation, knowledge of these various limitations is necessary to provide a sensible approach to the problem of particle analysis.

Some of the major factors which affect the chemical analysis capability of the electron microprobe are:

(1) The size (volume) of material from which a chemical analysis can be made

(2) The precision and accuracy of the analysis

(3) The detection sensitivity for various elements

(4) The degree of specimen alterations due to exposure to the electron beam and vacuum environment.

These factors, dependent on the physical processes of X-ray excitation and the large variation in specimen types, all affect the minimum analyzable volume, which can vary from less than 0.01 cubic micron to greater than 1000 cubic microns. The error in the analysis can range from less than 1 percent to greater than 50 percent, the limit of sensitivity to element detection can vary from 10 to 1000 parts per million, and specimen alterations can vary from little or negligible change to almost complete deterioration. Some of the principal variables are discussed in greater detail below.

Incident Electron Energy

The energy of the bombarding electrons normally is, for various practical and theoretical reasons, held constant for a given probe analysis. The choice of beam accelerating voltage is dependent upon the spectral line analyzed and, in the case of simultaneous multielement analysis, is determined by the spectral line of shortest wavelength to be analyzed. The incident electron energy is variable in most electron microprobes from about 2 to 50 kV and its magnitude has a primary influence on the following:

Electron Excitation Volume. The electron excited volume can be roughly expressed in terms of beam diameter and the distance penetrated by electrons along the incident as well as lateral directions.

The size of the excited volume is a function of the range of the primary electrons and hence their accelerating potential, and also the critical excitation potential of the particular characteristic X-ray line utilized for the analysis. Two major dimensions, the depth and width, of the X-ray-producing volume have been measured experimentally as a function of accelerating potential and found to vary according to the well-established electron range equation:[2]

$$R = aE_o^n$$

where R is the electron range expressed as a distance times the sample's density and E_o is the primary accelerating potential. This range equation, suitably modified to take into account the electron energy required to produce the characteristic X-ray under investigation, has been used to calculate the volume contributing to the analysis through direct electron excitation. The important fact is that the volume contributing to the analysis is a rapidly changing function of accelerating potential and that the analysis of low-density specimens, with good spatial resolution, such as some types of air pollution particles, requires the use of low accelerating potentials. At an accelerating potential of 5 kV, the analytical volume in such a specimen is approximately three orders of magnitude smaller than that which would result from the use of an accelerating potential of 20 kV. Reducing the diameter of the electron probe at the low accelerating potential will further reduce the size of the analyzed volume and improve spatial resolution, although not nearly so substantially so as obtained by the reduction of the primary accelerating potential.

The above paragraph should be modified, since this may not be necessarily true for all preparations of air pollution particles. A more general statement would be that in order to preserve spatial resolution (see sections on microprobe analysis of particles), one must either use a short-range, low-voltage probe or study thin or widely dispersed specimens of small size. The use of low voltages for analyzers has been covered by Anderson[2] and by Anderson and Hasler[3], which, for certain specimens, have very high sensitivity. Hall[4], on the other hand, has some very convincing arguments in favor of high-voltage operation when examining thin sections of biological material. The important point is that, by proper specimen collection and preparation methods, samples that are similar to thin biological specimens can be produced from air pollution collections. This is precisely the case if one is interested in very small (less than 1 μ) particles and it is possible to disperse these particles (for example, in a thin carbon film) so that X-ray background from the substitute does not interfere with the analysis.

The effect of the critical excitation potential of the characteristic X-ray line of the element under study on the volume analyzed is important also and it can be shown that large increases in spatial resolution can be attained with respect to a particular element by using an accelerating potential close to its critical excitation potential. Although this technique produces very small analytical volumes for the element in question, it also produces the generally undesirable consequence that the characteristic X-ray emission of other elements of lower critical excitation potential studied in connection with the first element will come from comparatively large volumes resulting in the reported elemental analyses not representing the same volume. For example[2], at 11 kV a zinc analysis using the ZnK_α line (E_c = 9.66 kV) originates from a volume of about 2 μ^3, but at the same kV sodium analysis using its K_α line (E_c = 1.07 kV) originates from a volume of 75 μ^3. This situation can be improved by using the L_α line of zinc (E_c = 1.02 kV) and reducing the accelerating potential still further. At 5 kV the volumes contributing to the analyses of zinc and sodium as well as all the lighter elements will be about 2 μ^3.

From the above discussions it is clear that, generally, to attain the best possible spatial resolution in a bulk specimen while remaining within the bounds of X-ray emission microanalysis as commonly employed and yet maintaining the equality of the spatial relationships of the elemental analyses, the longest wavelength characteristic X-ray lines of the elements which are detectable should be used at the lowest accelerating

potential compatible with the other basic aims of the analysis. This consideration is especially important when dealing with the light elements ($Z < 12$) for which the critical excitation potential is low (of the order of 1 kV or less).

Investigations of the effects of such parameters as accelerating potential and critical excitation potential are necessary to demonstrate the maximum sensitivity obtainable when air pollution particles are examined.

Target Absorption. The amount of absorption of X-rays escaping from the sample increases as the accelerating voltage increases. Primarily, this is due to the greater depth of electron penetration, and, consequently, the correction factors required for quantitative analysis to account for absorption are also increased, thus decreasing the correction's accuracy.

Secondary Emission (Fluorescence). The percentage of secondary emission (caused by the continuum) as compared with that of primary emission increases with the incident electron beam energy, thus increasing the total X-ray excitation volume and decreasing the accuracy of corrected intensity data for quantitative analysis.

Signal-to-Background Ratio. The signal-to-background ratio, which affects the minimum level of element detectability, initially increases as the accelerating voltage, E_o, exceeds the critical excitation energy, E_c, of a given spectral line, and then decreases for large values of the ratio, E_o/E_c.

Electron Background. Total electron background (single or multiple scattered electrons) increases as the accelerating voltage increases. Since it contributes to the measured background of the X-ray detection system, the minimum level of detectability is reduced.

Specimen Surface Conditions. A very complete understanding of the nature of the surface of a specimen is necessary for the proper interpretation of measured data. High accelerating potentials cause greater electron penetration and decrease the sensitivity of the analysis as far as surface conditions are concerned. This decreased sensitivity is, of course, highly dependent on the magnitude of absorption which the excited X-rays undergo and can be negligible in the case of a very-high-absorption situation.

Specimen Characteristics

Characteristics of the specimen may be the most important controlling factor(s) in the analytical capabilities of the microprobe. Some of the important characteristics include:

Density. For a given accelerating voltage and analyzed spectral line wavelength, the extent of electron penetration is determined by the density of the bombarded region.

Conductivity. The thermal and electrical conductivity of the specimen determines the stability of the electron beam and the ability to withstand the total energy in the incident beam without deterioration.

Distribution of Element Analyzed. A large concentration of the element being analyzed in regions surrounding the bombarded region is a very significant factor affecting the minimum detectable limit.

Spectral Interferences. The presence of other elements, which produce spectral lines that interfere with the desired element analysis, is a very significant factor affecting the minimum limit of detectability. Misidentification can occur when lines from two different elements in the sample appear at the same wavelength position in the spectrum. One example of this is the near coincidence of Ti K_β and V K_α.[2] A much more common case is the superposition of a higher order reflection of some shorter wavelength line over the first order of a longer wavelength line. Examples of this are the fourth orders of Cu $K_{\alpha 1}$ and Cr $K_{\beta 1,3}$ which coincide with first-order P K_α and Al K_α, respectively. These problems are minimized with spectrometers of good resolving power. The second of these problems can also be attacked using pulse-height selection to eliminate the higher energy, shorter wavelength X-rays. Misidentification might also occur if proper attention is not paid to line shifts due to chemical bonding and to the resolving of doublets in their higher order reflections. In addition to the above, the accelerating potential used during the spectrum survey is very important, as it limits the lines which can possibly appear and changes the intensity relationships between the various spectral series. Obviously, no lines of an excitation energy greater than the accelerating potential utilized can be present in the spectrum, and as the excitation energy of a spectral series is approached, the intensity of the series is diminished relative to the intensity of the spectral series of lower excitation energy.

Chemical Reactivity. The reactive nature of the specimen can be a controlling factor in the analysis capability to the extent that it creates spectral interference and masking absorption conditions. For example, in the analysis of oxygen in a specimen exhibiting surface oxidation, the presence of the oxygen in the oxide obviously masks the oxygen content of the specimen as well as contributing to a high absorption of the oxygen X-rays.

Specimen Size and Preparation. The application of existing correction formulae or the use of standards in determining quantitative chemical analysis requires a polished, flat surface. Restrictions for obtaining this condition due to the heterogeneous nature (chemical and/or mechanical) of a specimen play a significant role in the accuracy of quantitative analysis. The size of the specimen is of obvious importance when it is the same order of size (or smaller) as the exciting electron beam, e.g., submicron particle.

Instrument Limitations

The following are the most significant instrument factors limiting the analysis capability by the microprobe method:

Focused Beam Size. The minimum usable diameter of the focused beam for X-ray analysis is limited by mechanical design compromises necessary to incorporate X-ray spectrometers and light microscope systems for the analysis of opaque specimens. The minimum diameter is about 0.1 to 0.5 micron at 20 kV. At low accelerating voltages, below approximately 5 kV, the thermal spread of the thermionic emitting source greatly affects the minimum beam diameter because of the chromatic aberration sensitivity of magnetic lens focusing, and very small beam sizes generally cannot be obtained.

Probe Current Density. The current density of the focused beam is determined by the brightness of the electron source, the stability of the lens and accelerating-voltage power supplies, the spherical aberration of the final demagnifying lens, and the spread in thermally emitted electrons from the source. The limiting factor at the present time, from a practical point of view, is the brightness of the emitter source.

X-Ray Analysis System. Dispersive Type. The efficiency of X-ray detection and selection varies with the spectral line analyzed and is dependent upon the mechanical precision of the spectrometer, the perfection and efficiency of the analyzing crystal, the type of spectrometer, and the efficiency of the X-ray detector. The basis for dispersive spectrometer design is a practical compromise for the requirements of efficient X-ray detection for the total spectrum of X-rays generally analyzed, i.e., 1 to 100A.

Energy-Dispersive Type. Energy-dispersive X-ray analysis can be carried out using solid-state lithium-drifted silicon detectors in conjunction with multichannel pulse-height analyzers. The performance of this type of X-ray spectrum analyzer is limited by the energy resolution of the detector, the maximum counting rate of the detector/electronics system, and the minimum photon energy it is capable of detecting. It may be used for high concentration levels of element analysis, but its poor signal-to-background performance limits its usefulness for low-concentration analyses. However, its higher efficiency for photon collection and its ability to analyze the complete spectrum (lower limit of about 4A) simultaneously can, in certain cases, substantially decrease the time of analysis. This efficiency also can be an overriding factor in determining which type of detection system to employ (dispersive or energy-dispersive) in the measurement of low signal levels where background is not predominantly of the X-ray type (see following item). This is an important consideration in the examination of air pollution particles and may point the way to use of a scanning electron microscope equipped with an energy-dispersive detector as a way of investigating very small particles. This will be discussed in detail in a later section. Use of energy-dispersive detectors of the gas-flow proportional type can also be used in a similar manner for low-energy photon detection that is inaccessible to the solid-state detector, i.e., greater than 4A.

Noise Level. In the analysis of low X-ray intensity signals, two factors which can restrict measurement precision – and which are not related to the physical processes involved in the electron beam/target interactions – are electronic noise and cosmic radiation. Electronic noise may be related to random pulses caused by limitations in the X-ray detector/preamplifier system. The degree to which cosmic radiation interferes is dependent upon the amount of shielding present. With little shielding, a

count-rate level of approximately 0.3 cps can be experienced. Instrument location in the center of a large building (preferably, the basement), could reduce this level to 0.1 cps or less.

Microprobe Analysis of Particles

From the preceding discussion, it is easily seen that spatial resolution and detection sensitivity are extremely important topics, considering that the basic goal of microanalysis is chemical analysis of the smallest possible volume with the greatest possible sensitivity. The pursuit of this ideal is important, especially, in the field of small air pollution particles where the microstructures of interest are generally much smaller and their spatial interrelationships more complex than those most commonly investigated in the other fields of electron probe application. Spatial resolution[2] is determined by the volume of the specimen which, through excitation by the primary electron beam, contributes to the analysis. Detection sensitivity is commonly considered in two categories. The absolute detection limit gives the smallest number of atoms, commonly expressed in grams, necessary for the analysis. The weight fraction or relative detection limit describes the smallest fraction by weight detectable in the sample irrespective of the volume analyzed.

The weight-fraction detection sensitivity of an element is determined by the intensity of the characteristic X-ray line of the element utilized for the analysis and the intensity of the background radiation associated with the characteristic line. These intensities integrated over time are dependent, as mentioned previously, on the accelerating potential used, the primary electron beam current, the efficiency of the X-ray crystal and detector used in the X-ray detection system, and the matrix in which the element is found. The weight fraction detection limit is defined here as the concentration of the element that is required to produce an X-ray intensity greater than the intensity of the background at the position of the analytical line by an amount equal to three times the standard deviation of the background intensity. The absolute detection limit is determined by the weight-fraction detection sensitivity and the mass of material excited.

In light of the previously stated ideal of detecting the smallest number of atoms of an element in the smallest possible volume, it is of primary importance to consider the absolute detection limit that is the analytical definition of this ideal. The absolute detection limit is the smallest number of atoms of the element required for the analysis and is calculated by multiplying the weight-fraction detection sensitivity by the product of the excited volume of the sample and the sample's density. The size of the excited analytical volume, which is a function of the range of the electrons and therefore of the primary accelerating potential as discussed above, plays a dominant role in determining the number of atoms detected, with the result that those general conditions that produce the best spatial resolution also contribute to the best absolute detection limits.

The choice as to which of the characteristic X-ray lines of an element to be employed in a particular investigation should be carefully considered in light of the detection sensitivities achievable with each line. Each characteristic line of an element will in principle have a different detection sensitivity as the accelerating potential, sample composition, and efficiency of the detection system for each line are changed.

Two basic questions may be asked in an elemental analysis. The first question is qualitative and seeks the elements present. The second question, predicated on the first, is quantitative and seeks how much of each of the elements is present. A qualitative analysis by X-ray emission, therefore, depends on correctly identifying the lines of the characteristic X-ray spectrum as to their source elements, while a quantitative analysis depends on an accurate measurement of the X-ray line intensities as related to a reference standard of known composition. A qualitative analysis is, therefore, accomplished by examining the X-ray spectrum of the specimen and comparing the wavelengths of all the characteristics lines present with one of the several available reference compilations of X-ray wavelength versus elemental atomic number. Since the microprobe has crystal spectrometers which through suitable gearing give the wavelength directly in angstrom units, or in any case, since the wavelength is easily derivable from the θ angle, this task becomes one of simply comparing the wavelength reading of the peak of the spectral line with the reference list in order to identify the element that is responsible for that particular line. In most cases this is rather easy, considering that the X-ray spectra of the inner shell transitions are comparatively uncomplicated.

In this way, information about a number of elements suspected of playing an important role in the chemistry of the sample can be quickly obtained. In the general case, when a complete qualitative analysis is desired, the X-ray spectrometers are run through the complete wavelength range so as to detect as many of the elements present in the sample as possible. The practice of surveying as much of the wavelength spectrum as possible is a good one to adopt even for so-called known samples. Once the complete spectrum has been recorded the problem of identifying the source elements may be attacked by identification of the individual lines.

General Aspects of Particle Analysis

The microprobe is capable of providing chemical information from particles which in many cases is beyond the limitations of other analytical methods. For example, this situation may be true when

- The sample size is very small
- The analysis of individual particles is desired
- Nondestructive analysis is required
- Increased sensitivity and accuracy in the detection and analysis of minor constitutes is necessary
- The valence state of the elements, i.e., the state of chemical combination, is important
- Improved quantitative analysis is required.

The capability of most overriding importance is that of mass sensitivity, i.e., the ability of derive useful information from material of microgram quantities or less. This capability provides the basis for identifying constituents in a specimen which, in a

macrosample, occur in very low average concentrations but, in a microsample, occur in a percentage amount which fluctuates from high to low values. The points to be considered for detecting such "needles in the haystack" and characterizing them within the limits of the microprobe method are discussed below. In this discussion, the particles being sought are assumed, for the sake of simplicity, to be composed of a single element. The arguments presented can be easily extended to the multielement case using the weight fraction of the element being analyzed as a modifying factor.

Definition of Analysis Sample

The first point to be determined is the sample size (as distinguished from particle size), which must undergo analysis to provide the desired information. This determination requires a definition of the minimum number of particles which will give a satisfactory statistical representation of the total particle aggregate. The definition must take into account the relative occurrence of the particle types of interest. In this respect, the minimum sample then will be defined by the particle type which occurs least frequently and should include a number of such particles. Arbitrarily, for the purposes of discussion here and below, ten such particles will be considered sufficient for statistical purposes. Thus, if the least frequent particle type of interest occurs once in n particles, then the minimum number of particles requiring analysis is 10n. If the frequency of occurrence of a given particle type is unknown and is the information being sought, then an assumed minimum level that is based on some practical criteria must be used. In so doing, the criteria used must recognize the complexity and cost of the analysis. In the event that the number of particles is limited, i.e., below the 10n required, then the statistical characterization of the aggregate will of necessity be determined by the total number available.

The above comments point out one of the major problems associated with particle analysis; that is, the detection of a minor constitutent requires the analysis of a very large number of particles. For example, if a constituent is being sought which occurs once in every 10,000 particles, the analysis of 100,000 particles is required. Although individual analysis of all particles is not necessary, the analysis will in any event be very repetitive in nature, thus making it advisable to pursue automated procedures. The possibility of sample treatments that will concentrate the particle types of interest should also be evaluated thoroughly in the event that analysis cost is excessive. Also, the possible use of other techniques for pinpointing certain particle types should be pursued, e.g., detection by luminescence behavior under electron bombardment (visible, infrared, ultraviolet).

Specimen Preparation

The preparation of particles for microprobe analysis can be carried out in several different ways; for example:

- Metallographic mounting, in which the particles are embedded in a resin binder material such as bakelite or epoxy (limited to fairly large particles)

- Briquetting, in which the particles are compressed to yield a dense composite (when a large number of particles are available)

- Substrate mounting, in which the particles are placed on a substrate and affixed to it by the use of collodion or a vacuum evaporated coating

- Carbon-film embedding, in which the particles are placed on a near-dry collodion-amyl acetate film, carbon coated, and the collodion film dissolved.

Of these methods, metallographic mounting is best from an analysis standpoint but is limited to particles of a few microns in size or larger and materials that are not soluble in resins. Where this mounting method is applicable, quantitative chemical analysis can be successfully carried out using standard correction procedures. Briquetting is useful for submicron-size particle aggregates where quantitative analysis on a micron scale is desired, sufficient specimen material is available, and the analysis of constituents of very low concentration is not required. Substrate mounting or carbon-film embedding is necessary when the amount of sample material is limited, the mechanical alteration of the particles is not allowed, the identification and analysis of individual submicron particles is required, or when only qualitative or semiquantitative chemical analysis is needed. Carbon-film embedding may be necessary to provide good thermal contact for dissipation of heat generated by the beam, and, in addition, it provides maximum sensitivity to the particle analysis through the reduction of X-ray background and electron diffusion. The factors affecting the particle density per unit area for optimizing the efficiency of the analysis problem are discussed further below.

Single-Particle Detection Limits

One aspect of particular concern in particle analysis is the size of the smallest particle that can be detected as well as the ease with which the detection can be accomplished. Many factors must be considered to answer this question including the photon excitation rate produced by the probe, the composition of the particle in question, the photon-detection efficiency of the spectrometer, the background level, and the statistical character of photon production and measurement. The discussion in the remainder of this section will cover these points, with the exception that only pure-element particles will be considered.

Typical Instrument Performance.[5] Consider a target of copper bombarded by a 30 keV electron beam of a current density equal to 100 amperes/cm^2. This current density is equivalent to 0.1 μa in a 1-micron-diameter beam and is representative of typical microprobe operation. (This current density can be increased by a factor of about 5 if all conditions are optimized.) Under these conditions, a Cu Kα counting rate of about 100,000 cps can be measured by a focusing-type dispersive spectrometer with a peak to background of about 1000. Assuming the excited volume is about 3 cubic microns, then the counting rate that would be measured from a cubic particle of 0.1-micron dimension will be 30 cps. In other words, if a copper particle of this volume were bathed in an electron beam under the conditions given and no X-ray background was produced by the electrons not striking the particle, the counting rate of 30 cps would

be recorded by the spectrometer. A copper particle of this volume represents approximately 10^{-14} grams. This calculation provides an indication of the practicality of detecting particles in the submicron-size range. Thus, the experimentally measurable counting rate per picogram of copper, using a dispersive focusing spectrometer for the conditions stated, is approximately 3000 cps. The dependence of counting rate per picogram on critical excitation and accelerating voltages, spectral series, and specimen density has already been discussed.

Probe Diameter and Current Density.[6] The question of the improvement that can be obtained by reducing the probe diameter deserves comment at this point. In this respect, it should be noted that, for a fixed electron-source brightness and spherical aberration constant of the final probe forming lens, the maximum current obtainable in the focused probe is proportional to the 8/3 power of the probe diameter. Thus, the current density varies directly with the 2/3 power of the probe diameter. This circumstance thus will decrease the estimated counting rate given above if the probe diameter is decreased and will increase it if the reverse is true. Three additional factors affecting the most useful probe size are (1) the ability of the prepared specimen to dissipate the heat generated by the beam, (2) the X-ray background generated by electrons not striking the particle of interest, and (3) the real particle density of the prepared specimen. All of these factors are controllable, at least to some extent, by specimen preparation procedures. It should be noted that, although the probe current density varies directly with the 2/3 power of the probe diameter, the 8/3-power dependence of the total current on the probe diameter will cause the X-ray background – from other than the particle of interest – to increase in the same manner, i.e., 8/3 power. Thus, any benefit from increasing the current density can be realized only if conditions for minimizing this background are rigorously adhered to. Finally, it should be mentioned that improvement in the typical brightness of the electron source and spherical aberration of the final probe forming lens are possible but involve major design innovations in current microprobe instrumentation.

Energy-Dispersive X-ray Detection.[7] In the above discussion, the X-ray detection system was assumed to be a dispersive-focusing-spectrometer type. The use of an energy-dispersive X-ray detection system could, in certain cases, allow an increase in the efficiency of total X-ray counting by a factor of 10 or more. Energy-dispersive systems using solid-state, lithium-drifted silicon detectors are limited in their total count-rate capacity (energy resolution decreases with counting rates above about 25,000 cps). In addition, their peak-to-background performance in the measurement of X-rays from pure elements is quite low, varying from 5 to 25 in the wavelength range 1 to 4A. Recent availability of solid-state detectors, with a factor-of-2 improvement in energy resolution, should increase these peak-to-background values also by a factor of 2. Energy-dispersive detectors of the gas-flow proportional type have poorer photon-energy resolution above 3 keV (4A). Below this energy, however, their resolution can be comparable or better. The relative mechanical simplicity of the gas-flow type compared with the solid-state type is also a favorable practical characteristic.

It should be noted that the peak-to-background characteristic of the dispersive focusing spectrometer may not be applicable at low counting rates. Under conditions where the X-ray signal is 10 cps, a calculated background-count level of 0.01 cps would be obtained if a 1000 to 1 peak-to-background ratio applied. Since the cosmic radiation background can be 0.3 cps if little shielding is present, the effective peak to

background is reduced to 33, thus making the dispersive and nondispersive systems comparable in this respect. The higher photon-collection efficiency of the energy-dispersive system may thus be quite practical in certain aspects of particle analysis.

Hall[8] has also commented on the possibility of favorable energy-dispersive detection using very small probe diameters (0.1μ to 0.03μ) and thin samples. This could be the case if a scanning electron microscope equipped with an energy-dispersive detector were used on an air pollution sample suitably dispersed on or in a material of low X-ray background. The lower elemental resolution would still be a major limitation, however.

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